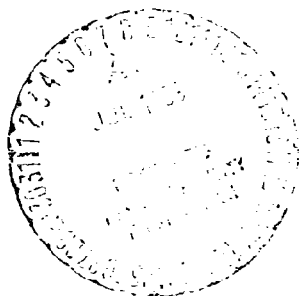


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CHEMICAL CONCENTRATIONS OF POLLUTANT LEAD AEROSOLS,
TERRESTRIAL DUSTS, AND SEA SALTS
IN GREENLAND AND ANTARCTIC SNOW STRATA

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ABSTRACT

In this study we report analyses of lead in annual ice layers from the interior of northern Greenland and in annual layers of ice from the interior of the Antarctic continent. We show that lead concentrations increase from $<0.001 \text{ } \gamma \text{ Pb/kg ice}$ at 800 BC to $>0.200 \text{ } \gamma \text{ Pb/kg ice}$ today in north polar ice sheets, the sharpest rise occurring after 1940, and that the levels of lead in south polar ice sheets are generally below our detection limits before 1940 and rise only to about $0.020 \text{ } \gamma \text{ Pb/kg ice}$ after 1940 (in this paper the symbol gamma, γ , means microgram, 10^{-6} gm). The increase of lead with time in north polar snows is ascribed mainly to lead smelteries before 1940 and to burned lead alkyls after 1940. The difference between the concentrations of lead in northern and southern polar snows is ascribed to barriers to north-south tropospheric mixing which originate from meridional circulating cells and which hinder the migration of aerosol pollutants from the northern hemisphere to the Antarctic.

Our observations of the chemical concentrations of the common elements in ice from the interior of Greenland and Antarctica can be explained in terms of simple relations among sea salts and terrestrial dusts. We found about ten times more dust in Greenland interior ice ($35 \text{ } \gamma/\text{kg}$) than in Antarctic interior ice ($\sim 2 \text{ } \gamma/\text{kg}$), but found twice as much sea salt in Antarctic interior ice ($110 \text{ } \gamma/\text{kg}$) than in Greenland interior ice ($67 \text{ } \gamma/\text{kg}$). We found that the proportions of sodium, chlorine, magnesium, calcium, and potassium adhered closely to sea salt ratios in ices that were relatively free of silicate dusts, even when the concentrations of sea salts decreased from $1100 \text{ } \gamma/\text{kg}$ in NW coastal Greenland ice to $110 \text{ } \gamma/\text{kg}$ in Rockefeller Plateau ice in the Antarctic interior. We also found that the amounts and chemical composition of silicate dusts in

Greenland were no different in coastal and interior ices, averaging 3 γ Mg, 5.6 γ Ca, 2.0 γ K, 0.1 γ Ti, and 6.8 γ Si per kg ice respectively in the interior. We found that there are seasonal variations in the amounts of pollutant lead, sea salts and silicate dusts in the snows, pollutant lead and sea salts being two or three times more concentrated in winter than in summer snows, while silicate dusts were three times more concentrated in spring than in winter snows. The above interpretation, which unifies all the data, is consistent with most related chemical and meteorological observations at temperate latitudes.

INTRODUCTION

The upper layers of the oceans seem to be polluted with industrial lead. Off-shore from industrial areas, surface waters show much higher lead concentrations than deep waters (TATSUMOTO and PATTERSON, 1963a,b), and this effect becomes diminished in the open oceans (CHOW and PATTERSON, 1966). Although lead seems to be entering the oceans by means of rivers at greater rates today than has been common in the past (CHOW and PATTERSON, 1962), the burning of lead alkyls in automotive fuels has become so extensive that a major fraction of industrial pollutant lead in the oceans probably originates from the direct washout by rain of industrial lead aerosols in the atmosphere over the oceans (TATSUMOTO and PATTERSON, 1963a; CHOW and PATTERSON, 1966).

The burning of lead alkyls is an efficient method of introducing lead aerosols into the atmosphere and this practice first began within the United States in 1924. If today this serves as an important means of introducing lead into the oceans, lead should have increased markedly in the atmosphere of the northern hemisphere after 1924. One way of finding out whether lead pollution in the atmosphere did increase with time is to analyze the precipitated lead in successive annual layers of old preserved snow (GOLDBERG, 1963). The ancient annual layers of snow which are preserved in temperate region glaciers are excessively thick and are both saturated with percolation water and mechanically mixed when rapidly sluiced down glacial inclines. In addition, temperate glaciers are much dustier than polar ice sheets, and since those dusts contain natural lead, the effect of atmospheric lead pollution might be masked. Only the quiescent ice sheets in the arid, perpetually frozen polar regions of the earth provide annual layers of precipitation that are undisturbed by percolation and mechanical mixing, that are relatively free of dusts and salts, and also are thin enough to be accessible even when centuries old.

JAWOROWSKI (1967) found lead concentrations in ice from two small Polish glaciers to increase by a factor of ten during the past century, but concentrations in the latest ice layers were startlingly high : 80 to 150 γ Pb/kg. It is unlikely that such lead concentrations are typical of those in temperate latitude snows of the northern hemisphere because they exceed the 40 γ Pb/kg concentrations commonly found in urban rain (CHOW and EARL, 1968a; LAZRUS et al., 1969), and the 2 γ Pb/kg concentration found in new-fallen snow in a primitive area 160 km NNE of San Francisco (TATSUMOTO and PATTERSON, 1963b). The observations of lead in polar and Polish ices probably represent the extremes of general and local significance respectively.

The concentration of lead in snow will vary according to different meteorological situations, and it is insufficient to show only that lead increases with time in the annual layers, for this could result from a number of different factors, some of them unrelated to general increases of lead in the atmosphere. A lead increase in snow can be related to atmospheric concentrations with more confidence if it can be shown that the background of sea salts and dusts in the ice remains steady, so we measured the chemical concentrations of Na, Cl, Mg, Ca, K, Ti, and Si by isotope dilution, neutron activation, atomic absorption, emission spectrography, and colorimetric spectrophotometry, using two methods for each element in most cases.

We found, contrary to observations of a number of other investigators, that polar ices are extremely pure, being nearly equal to the purest laboratory water. This made the determination of salts and dusts difficult, because the samples corresponded to waters normally used for blanks, and it became necessary to scale up sensitivities by factors of hundreds without losing too much accuracy. Iron and related elements could not be studied because stainless steel tools had

been used in the ice collection procedure. The snow in some of the youngest samples had formed in air which contained traces of an oily smoke. Such samples may have suffered dust losses because a minute oil impurity scum which had incorporated portions of the dust, had separated out from the melted ice blocks, and had adhered to the walls of the melting drums. Water samples were aged as much as 24 months in polyethylene carboys before suitable analytical methods for metals other than lead were developed and applied, but this seems to have introduced no serious errors.

Other investigators, who have studied polar ices, have published values for common element concentrations that are either grossly higher than ours or are so different they cannot be explained by the simple relations mentioned above. Such data have been interpreted in a variety of ways, invoking gross chemical fractionation of sea salts or the gross addition of either silicate dusts or sea salts. We believe that most of the conflicts among chemical data published by different investigators can be explained by contamination.

It appears that the single most important factor affecting contamination is the manner of collecting the ice samples. The extreme precautions that we had to take against lead contamination and the excessive size of the samples that were required for the lead analyses fortunately dissuaded us from attempting to use drill core material (which is highly contaminated) and seems to have automatically provided us with unusually clean ice samples that were well suited for analyses of common salts and dusts. We have therefore explained many factors in detail which might affect the lead content of the ice samples we procured, and have discussed our analytical methods at length. It is hoped that these details, not normally given, will provide a rational basis for criticism of our and other investigator's work, and will help resolve some of the conflicts that presently exist regarding the geochemistry of polar snows.

SAMPLE COLLECTION

Location and character of sites

Three types of sites were used in order to study a maximum number of annual ice layers. We could not use cores from deep drill holes since we required large amounts of ice for lead analysis. Instead, we mined the ice from walls of shafts. It was not logistically feasible to dig deeper than several hundred layers into the ice sheet, so we used ice from existing tunnels driven into the edges of old glaciers for the most ancient samples. Again, it was not logistically feasible to dig a shaft that penetrated several hundred annual layers at a virgin location. Instead, we used existing shafts or dug them ourselves at contaminated permanent operational bases and refrained from taking samples from the upper layers at those locations. We then dug shallow trenches and shafts at virgin sites remote from the contaminated sites to sample the uppermost layers of ice and snow.

In the north, samples were collected in the vicinity of Thule, Greenland, which lies on the northwest coast of the island. Inland and SE from Thule, over 19 km of rocky moraine, lies Camp Tuto (Thule takeoff ramp). Near there the Glet Gletscher has a stagnant edge and ice blocks were collected from the walls of a horizontal tunnel driven into it. Nearly two hundred km E of Thule, on top of the Glet Gletscher, lies Camp Century (one hundred mile base), a former year-round American base. Near there, firn and ice blocks were collected from the walls of an inclined shaft driven down into the glacier. At a virgin site 80 km further ESE of Camp Century, firn blocks were collected from the walls of an open trench dug into the surface of the glacier.

In Antarctica, ice was collected from a small ice tongue projecting from the flanks of Mt. Erebus on Ross Island. Ice was also taken from the walls of a horizontal tunnel driven into the tongue of a small glacier in Wright Valley,

which lies in an arid, ice free land 110 km NNW of McMurdo Station, the main American base in Antarctica. At New Byrd Station, a year-round American base near the center of the large Antarctic plateau facing the South Pacific, firn blocks were taken from the walls of the lower portion of an inclined shaft driven down into the glacier. At a virgin site 215 km ENE of New Byrd Station, firn blocks were taken from the walls of an inclined shaft driven through upper firn layers.

Camp Tuto is located at $76^{\circ} 25' N$, $68^{\circ} 20' W$. Near there, ablation of the west edge of the Gret Gletscher is balanced by accumulation and outward flow, so that edge is only slowly receding. In the winter, the bare rocky strip along the coast is covered by snow and ice so that local dust transport is minimized. In the summer strong winds stir up much dust in this region, but the dense air masses near the ice surface flow westward with high velocity down the sloping inclines of the glacier, blowing local dust away, not toward, the glacier. Although the forward edge of the ice cliff shows a thin morainal coating, the interior is composed of impermeable, clear blue ice. The ice sheet is approximately 76 meters thick at this location.

During the period 1955 to 1957 a 400-meter tunnel together with some large chambers was excavated by military personnel back into the glacier from the cliff face, at a level approximately 21 meters above the floor of the glacier. The orientation of gravel, sand, and silt bands that were intercepted showed that rocky materials from the bottom were riding up into the ice along a shear plane aligned parallel to, but dipping steeply away from the extreme forward edge. At a given level the coarseness and abundance of these materials decreased rapidly further back into the glacier, so that at 300 to 400 meters in from the cliff edge they were sharply confined to the lower portions of the ice (RAUSCH, 1959).

During 1958 and 1959 a new tunnel system had been excavated at a level 30 meters above the old tunnel and 300 meters to its side (ABEL, 1961a). The new main tunnel ended 364 meters back from the ice cliff face, and the rear half was in clear blue ice completely free of any visible traces of silt or color except for one small isolated gravel pocket at the end of the tunnel. The rear half of the tunnel was 50 meters above the floor of the ice and 30 meters above ice that contained traces of silt.

Our samples were taken 275 meters in from the portal entrance and 10 meters along the north wall of the right-hand drift, or "personnel room" next to the "location 1" site previously sampled for C^{14} by OESCHGER et al. (1966). The age at that point was found by them to be 2800 years. Our ice sample consisted of a mixture of young and old ices whose age spread is unknown. OESCHGER et al. (1967), found the ice to be about 5000 years old at "location 2", a point about 100 meters nearer the tunnel mouth, in agreement with the orientation of inferred shear planes and stratigraphic age trends. Accordingly, ice layers of different ages do not seem too badly mixed.

Leaded fueled trucks were driven within both tunnels, and in connection with the activities for which the tunnels were designed, leaded gasoline was stored in an ice sump in the old tunnel, while sewage and bulk oil were stored in the new tunnel. Our collection site was 300 meters away and 30 meters above the leaded fuel sump, 30 meters away from the sewage room, and 70 meters away from the bulk oil room. Ice closure had reduced chamber cross sections to less than half of their original area by the time we took our samples in 1965, but engulfment of contaminated ice occurred mainly at the corners, while the material behind the center wall surfaces was virgin ice protruding inwardly (ABEL, 1961b). The surface of the ice within the Tuto tunnel was

undoubtedly severely contaminated with industrial lead, but the ice was completely impervious, and we are confident that 20 cm of ice provided a complete barrier against lead contamination.

Camp Century was located at $77^{\circ} 10' \text{ N}$, $61^{\circ} 08' \text{ W}$ at an elevation of 1886 meters in a percolation facies zone (BENSON, 1962) on the westward facing slope of the Grot Gletscher. Inglefield Bay was 120 km west of Camp Century, while the shores of Melville Bay were 120 km south. Both of these bays are unfrozen in the summer. The ice is 1387 meters thick at Camp Century (HANSEN and LANGWAY, 1966). The surface is moving WSW at about 10 meters per year (MOCK, 1968a). Virtually all air masses at ground level come to Camp Century from the ESE sector, which is the virgin interior. The present accumulation rate, after vapor ablation, is $35 \text{ gms H}_2\text{O/cm}^2 \text{ yr}$ (MOCK, 1968b; CROZAZ et al., 1966; CROZAZ and LANGWAY, 1966). Accumulation increases to the SE. Small refrozen melt-water horizontal lenses and vertical glands occur frequently in the firn and one essentially continuous refrozen melt-water layer for the year 1954 is prominent (BENSON, 1962). Percolation rarely penetrates deeper than several annual layers before it is refrozen.

The Camp Century region was virgin before World War II. After that time Thule became, in cooperation with the Danish Government, a major U.S. military air and defense base. Scientists made a half-dozen traverses through the region with leaded fueled vehicles after 1952 and before 1959. The locations of these traverses are known. Camp Century, which consisted of a series of buildings buried beneath the surface and connected by tunnels, was constructed in 1959-1960 (CLARK, 1965). It housed hundreds of men at a time. It was powered by an atomic reactor until 1964, when diesel generators were substituted. Maintenance against wall closure proved too costly, and Camp Century was abandoned

in 1966. It was supplied by leaded fueled aircraft and diesel fueled tractors operating from Thule and Camp Tuto in summer months. Many leaded fueled vehicles were used on the surface in the immediate vicinity of Camp Century and within its tunnels beneath the surface. Many scientific traverses to the east, north, and south began and ended at Camp Century. The locations of most of these traverses are known.

In 1963-1965 an inclined shaft was dug at Camp Century. Operations were conducted by U.S. Army engineers. It was inclined 20° below horizontal and was 300 meters long. The lower end was 100 meters, or approximately 212 annual layers below the surface. Two horizontal drifts leading from the base of the inclined shaft and three vertical shafts leading to these drifts were dug in late 1965, a few weeks after we had collected our samples from the inclined shaft. The upper third portion of the inclined shaft was excavated by an electric rotary power mill. The lower two thirds of the inclined shaft were excavated by electric hand chain saws. The three vertical shafts were excavated by steam drill.

We collected samples for preliminary work from the walls of the upper portion of the shaft in July and August, 1964. The samples studied in this report were taken during June and July, 1965, from nine levels between 14 and 100 meters within the shaft. Depth density curves (LANGWAY, 1967; MOCK, 1965) and accumulation data at Camp Century were used to assign ages to these sample levels. Pb^{210} determinations of the average ages of the upper layers (CROZAZ and LANGWAY, 1966) agreed with these assignments. The oldest measured Pb^{210} age was 112 years at a depth of 58 meters, while the age at this depth calculated from accumulation and compaction was 108 years.

The youngest annual layer we sampled at Camp Century, 1946, was 6

annual layers beneath the lowest annual layer that might have been contaminated by local vehicular exhausts. The center of the Camp Century subsurface sewage lake, which contained about 1.5×10^7 liters of unfrozen sewage in 1965, was located 600 meters away from the inclined shaft, and had a horizontal contamination spread of less than 60 meters from the center. It did not penetrate below 50 meters (RODRIGUEZ, 1964). The concentration of industrial lead in this material was 10^6 times greater than the concentration of natural lead in Camp Century firn and ice. The subsurface unfrozen heat exchange lake for the atomic reactor was about 400 meters from the inclined shaft. The nearest subsurface unfrozen potable water lake was about 300 meters from the inclined shaft. The subsurface liquid radioactive waste dump from the atomic reactor was about 250 meters from the inclined shaft.

Army engineers who excavated the shaft smoked profusely and consumed large quantities of carbonated beverages which came from cans that had been sealed with lead solder. The persons were therefore ingesting and excreting large quantities of industrial lead. In addition to blowing their noses and spitting on the walls and floors of the shaft, they also urinated on the walls and floors of the shaft. The concentrations of industrial lead in these body excretions were about 100,000 times greater than the natural concentrations of lead in the firn or ice at Camp Century. Their clothing had been heavily exposed to the fumes and surfaces of vehicles burning leaded fuels. A single fiber or particle of hair, skin, or clothing could readily contribute more industrial lead than would be contained naturally in all of the firn or ice collected from one sample level in the shaft. It is believed that the motor housings and auger troughs within the shaft were primed with lead-based paints. This paint was chipped off liberally during use in the shaft. A well-used lead hammer was found in a tool box at the head of

the shaft. Lead soldered electrical wires and connections were used in the shaft. Warming huts were electrically heated, but a high-capacity diesel-burning space heater was used occasionally near the shaft head for engineering tests. Although the shaft exited to the surface, the principal access was from a sub-surface tunnel connected to the Camp Century tunnel complex.

The permeable firn zone ended at about 65 meters depth at Camp Century (S.J. MOCK and A. J. GOW, personal communication). Six samples younger than 1835 were collected from the permeable firn of the inclined shaft, but we believe it unlikely that atmospheric pumping, brought about by pressure changes, would mix aerosol contaminants through more than a few centimeters of permeable firn because it is an effective filter. It has been suggested that snow is ineffective as an aerosol filter (ANONYMOUS, 1962). Air was continually exhausted from the main tunnel complex, and this caused tunnel pressures to be negative with respect to air pressures within the tunnel walls, so that there was some forced streaming of air down through shallow depths from the surface and out tunnel walls. The inclined shaft was so far removed from these operations that these effects were probably negligible, however.

Except for small holes melted by urine that were easily recognized, the volume of mucus and urine expelled on the walls of the inclined shaft would be insufficient to penetrate more than ten centimeters of permeable ice. It was observed that large quantities of strongly dyed hydraulic fluid, when splashed on permeable shaft walls, penetrated less than five centimeters into the wall. Extended period air sampling filter tests for lead particulates greater than 0.01 micron in diameter showed about $2 \text{ } \gamma \text{ Pb/m}^3$ within the main tunnel complex, about $0.003 \text{ } \gamma \text{ Pb/m}^3$ within the inclined shaft, and about $0.0005 \text{ } \gamma \text{ Pb/m}^3$ in the air above-surface at Camp Century. The first two numbers originate from

filters collected by us in 1964 and analyzed by F. ROBINSON, Stanford Research Institute, Palo Alto, California. The last number originates from ROBINSON'S unpublished analyses of filters collected near Camp Century in 1965.

The Greenland virgin trench site (km 80) was located at $76^{\circ} 46' N$, $58^{\circ} 52' W$, at an elevation of about 1800 meters, in a percolation facies zone on the westward facing slope of the Glet Gletscher. The seacoast was 110 km away to the SW. It is inferred, from data at Site 2 and at Camp Century, that air at ground level usually came to the virgin trench site from a southeasterly direction. Using the available logs of all previous land traverses, the virgin site was located 40 km S. E, or W of any previous land traverse that used vehicles. A more southerly location was made unfeasible by expected increased accumulation. Accumulation, excluding vapor loss, was about $47 \text{ gm H}_2\text{O}/\text{cm}^2 \text{ yr}$. This number was calculated on the basis of depth-density relations at Camp Century, and the July 1954 melt-layer being located at a depth of 11 meters. Stratigraphy for the final year at several different local pits gave $40 \text{ gm H}_2\text{O}/\text{cm}^2 \text{ yr}$, assuming a density of 0.39. Refrozen melt-water lenses and glands occurred frequently in the stratigraphic section, and the refrozen 1954 melt-water layer existing near Camp Century was believed to have been identified in the stratigraphic section here.

The trench was rough-cut in late July, 1965, by a tractor snow miller and a tractor blade. The trench was 100 meters long and its floor sloped from zero depth at both ends to a maximum depth of 15 meters at the center. Spoils were accumulated beyond the ends. The entire sled train and its non-scientific personnel remained 300 meters downwind (NW) from the trench. Our samples were taken from five wall locations just above the floor of the trench.

Snow that had accumulated during the last year at the trench site

(August, 1964 to August, 1965) was collected in five separate, consecutive layers from a fresh, hand dug trench located 100 meters upwind (SE) from the main trench. The top 6 cm, which fell during a storm that occurred after arrival at the site and before the time of collection, was discarded (layer 0). The next 32 cm down, which contained soft, thick cross-bedded, coarsely crystalline snow interspersed with frozen melt-water and wind crusts, was labeled Midsummer 1965 snow (layer 1). The next 32 cm down, which contained snow of similar facies as that immediately above was labeled Spring 1965 snow (layer 2). The next 10 cm down, which contained massive, hard packed, thin bedded, finely crystalline snow, was labeled January Winter 1965 snow (layer 3). The next 10 cm down, which contained snow of similar facies as that immediately above, was labeled December Winter 1964 snow (layer 4). The next approximate 7 cm included the 1964 Autumn depth-hoar frost layer. It was about 2 cm thick, was vuggy, and contained vertically aligned macro-crystals that were underlain by a porous ice sheet less than a mm thick. This lowest 7 cm layer was labeled Autumn 1964 snow (layer 5).

The Spring 1965 snow (layer 2) was sampled halfway between Camp Century and the virgin trench site, (km 45), and at the outer periphery of Camp Century itself, (km 1). The Spring 1965 snow (layer 2) was 14 cm thick at Camp Century, and on one side of the pit it was observed that a boot-print had penetrated the upper 4 cm of the layer. The top of the footprint was truncated 3 cm above the base of the Midsummer 1965 snow (layer 1). Camp Century was reopened in May, for the 1966 summer season.

The ages of the samples collected from the virgin trench were determined by accumulation estimated from pit stratigraphy and by the location of the 1954 continuous, refrozen melt-water layer. The 1964 Autumn depth-hoar frost layer

was readily determined, but the location of this layer became less certain in deeper annual layers, and strong reliance was placed on finding at a depth of 11 meters, a continuous ice band, 2 cm to 5 cm thick, underlain by an unusually large series of ice glands and lenses. Ages were regularly assigned on this basis, allowing for compaction, irrespective of intermediate stratigraphy.

Before the samples were collected, the site was visited by a leaded fueled helicopter bringing tractor repair equipment. It flew in from the NW at ground level along the flagged sled train trail. It landed and took off downwind from the trench site. Diesel fuel was used exclusively in the camp and by the tractors. Drifted winter snow from regions contaminated by vehicle traverses may provide the greatest source of locally contaminated snow in samples from the virgin trench site. There can be no question but that some of the winter snows we collected drifted in from great distances away. It is emphasized that dilution effects, after a few tens of km, should make snow contaminated by a vehicle traverse indistinguishable from background snow in this region. Air sampling tests conducted at the virgin trench site did not show lead above a $0.005 \text{ } \gamma \text{ Pb/m}^3$ blank. This number originates from filters collected by us and analyzed by E. ROBINSON. The allowable air collection corridor between the trench and the camp was so narrow that storms and variable winds prevented the accumulation of larger volume samples that would have reduced this upper limit.

Erebus Glacier Tongue, located at $77^{\circ} 42' \text{ S}$, $166^{\circ} 40' \text{ E}$, is fed by a small glacier on the south flank of Mt. Erebus, a 3743 meter active volcano on Ross Island. It is about 2 km wide and projects out into McMurdo Sound for about 10 km. It is about 300 meters thick, and although it is intensely crevassed, and may partially float upon the sea, the tongue is permanent and ablates mainly from the seaward end. In the winter, it is surrounded by sea ice, and in the summer

by open water. There are bare patches of volcanic rock on the flanks of Erebus, and the blue ice in the glacial tongue contains scattered pea-sized to fine-grained fragments of volcanic rocks that are visible at a frequency of about one fragment for every 2 to 10 square meters of exposed ice surface.

Our sample of impermeable blue ice was collected from the upper portion of a crevasse wall just beneath the milky, surface-ablation layer. The site was about 4 km from the seaward end of the tongue. It was found to contain large concentrations of volcanic dusts and sea salts.

Meserve Glacier, located at $77^{\circ} 32' S$, $162^{\circ} 25' E$, is one of a series of small glacier tongues flowing down the southern flank of Wright Valley from a narrow accumulation ridge named the Asgard Range. In 1966, a horizontal tunnel with side adits was driven back into a cliff edge located near the lower tip by a glaciological party from Ohio State University (CARNEIN and BULL, 1968). The ice was about 35 meters thick at that location, and the tunnel was within the bottom few meters of ice. Our sample was taken from the wall of a side adit, about 25 meters in from the mouth of the main tunnel. It was found to contain large concentrations of silt and salts.

New Byrd Station, located at $80^{\circ} 01' S$, and $119^{\circ} 31' W$, is at an elevation of 1530 meters in a dry facies zone. The coast is 670 km to the N. The ice is 2164 meters thick at this location (GOW et al., 1968). The surface is moving WNW a few meters/yr (A. J. GOW, personal communication). Most air comes to New Byrd Station at ground level from the NE. The present accumulation, after vapor ablation, is $10 \text{ gms H}_2\text{O}/\text{cm}^2 \text{ yr}$ (GOW, 1965; CAMERON, 1969). In January 1966 Gow found January 1959 to be at 1.8 meters depth in a pit dug near the head of the inclined shaft. This observation agrees well with stake accumulation and Pb^{210} data. Accumulation increases

to the NE. Melt-water percolation is absent.

The New Byrd Station region was virgin until 1956, when the site for Old Byrd Station, 10 km W, was surveyed. After that time Old Byrd Station, and then New Byrd Station were constructed and occupied. Diesel fuel was used for power. Both stations were supplied by diesel fueled and leaded fueled aircraft, and numerous leaded fueled vehicles have been used in their vicinity. Many scientific traverses using leaded fueled vehicles and aircraft began and ended at New and Old Byrd Stations. The locations of most of these traverses are known.

In November and December, 1965, we dug an inclined shaft 1 km NE of New Byrd Station. The shaft was 90 meters long, and inclined below the horizontal at an angle of 30° . The lower end was 44 meters, or approximately 272 annual layers below the surface. The shaft was excavated by electric hand chain saws. An electric winch hoisted the ice block spoils out in a 1/2 ton capacity sled.

In January, 1966, we collected samples from 10 levels between 5 and 44 meter depths within the shaft. Depth-density curves and accumulation data were used to assign ages to these levels. Our density data were obtained from cores taken from the walls of the inclined shaft. Pb^{210} determinations of the average ages of the upper layers (WINDOM, 1968) agreed with these assignments. The oldest measured Pb^{210} age was 111 yrs at a depth of 20 meters, while the age at this depth calculated from accumulation and compaction was 109 yrs.

The youngest annual layer we sampled at New Byrd Station, 1942, was 14 annual layers beneath the lowest annual layer that might have been contaminated by local vehicular exhausts. The center of the New Byrd Station subsurface sewage lake was 1000 meters away from the inclined shaft. There were no other subsurface

unfrozen bodies of water nearby. (Water was supplied by a tank snow melter).

Leaded fueled aircraft twice dumped fuel aloft over New Byrd Station in 1965-1966. Except for this, no leaded fueled vehicles or personnel other than those working in the shaft came within 1 km of the location while it was being dug and sampled. The shaft was 1 km upwind of New Byrd Station and offset from its runway on the side opposite McMurdo Station. It exited to the surface and was not connected to the New Byrd Station tunnel complex. A diesel stove heated a warming hut on the surface near the shaft entrance. Materials containing leaded paints or alloys were excluded from the shaft. Working parties used new clothing relatively free of vehicle exhaust fumes, and ordinarily used a ladder entrance to New Byrd Station, rather than the vehicular entrance. Workers obeyed strict rules against bringing trash or liquids into the shaft and they used only designated toilets that were remote from the shaft.

The permeable firn zone extends to a depth of 57 meters at New Byrd Station (A. J. GOW, personal communication), so that all of our samples taken from the shaft were in permeable firn. Air sampling tests at the surface showed about $0.0004 \text{ } \gamma \text{ Pb/m}^3$. The air inside the shaft was not sampled, but unlike the results for the Camp Century shaft, the concentrations of lead in the air of the New Byrd Station shaft were probably equal to or less than outside air concentrations because we strictly controlled lead contamination.

The Antarctic virgin site was located at $78^{\circ} 52' \text{ S}$, $111^{\circ} 19' \text{ W}$, at an elevation of about 1750 meters in a dry facies zone. The ice is about 3000 meters thick at this location, and the coast is 450 km to the N. Accumulation is about $32 \text{ gm H}_2\text{O/cm}^2 \text{ yr}$, as calculated for January, 1956, being at a depth of 7.4 meters and using an average density of 0.43. The stratigraphy is questionable because of a problem year. Using a density of 0.37, the accumulation for

the period January, 1964, to January, 1966, is calculated to be $39 \text{ gm H}_2\text{O/cm}^2\text{yr}$. Accumulation for the last two years may be atypical, however. An accumulation of 32 to $39 \text{ gm H}_2\text{O/cm}^2\text{yr}$ conforms with extrapolations of stake accumulation data by BRECHER and CAMERON (1969). The site was located more than 30 km away from other traverses, using wind direction data at New Byrd Station and the available logs of previous land traverses.

The unexpectedly heavy accumulation necessitated the digging of an inclined shaft, rather than a trench. It was 30 meters long and inclined 30° below horizontal. It reached a depth of 13.6 meters, or about 20 annual layers down. It was dug with pickaxe and shovel. Our samples were taken at three levels between 3 and 13 meters within the shaft during January, 1966. In addition, the January, 1965, to January, 1966, year was divided into an upper half (Summer 1965 to 1966) and a lower half (Winter 1965), and sampled separately from a remote trench. The Winter 1965 layer was also sampled at km 125 (sample 66-6) and km 35 (sample 66-7), from trenches dug 3.5 km N of our sled trail.

Our sled tractor burned diesel fuel, and it contained a small diesel stove which burned continuously at the virgin site. Camp was 100 meters away from the inclined drift, but the wind shifted after operations had started, and the camp was upwind (S) of the inclined drift most of the time. The principal 1965-1966 summer sastrugi which we traversed along the entire trail had been formed by ground winds originating from the NE.

Cutting and handling the firn and ice blocks

Samples were not collected until after the shafts and trenches had been completely excavated. With few exceptions, the procedure for collecting sample firn blocks was the same at all sites. Near the collection site, the workers changed into clothing, mukluks and parkas that were initially new, that were never worn except during ice block collecting operations, and were

stored in plastic bags. They then put on disposable outer polyethylene trousers and hooded coats that had elastic wrist, ankle, and waist bands. These plastic garments were discarded after each working shift, and new ones were worn the next day. Workers also put on disposable polyethylene liners over knitted woolen gloves, and renewed these liners frequently during a shift as they became torn. Polyethylene sleeve guards with elastic bands covered the joint between the glove and the coat sleeve. Plastic boot covers could not be worn because they were too dangerous.

At each sampling level, and only immediately before sample collection, the wall of the shaft, adit, or trench was cut back with an electric chain saw, using no lubricant, for a distance of 40 to 80 cm. This cutting was done with an ice adze when electric power was not available. The debris was discarded. All tools used in subsequent operations were mainly of stainless steel that had been cleaned in successive washings and rinsings with ultra-high purity HCl and HNO_3 and water. Each tool was kept sealed in a polyethylene bag when not actually in use.

The back wall of the collecting alcove was cut back an additional 15 cm beyond any chain saw cuts with an ice adze, and guide holes for a SIPRE corer were located in it by means of a stainless steel template, equipped with a handle and spikes that held it steady, and a hand drill. SIPRE bore holes were drilled electrically or by hand to a depth of 50 cm in a network such that the corners of the blocks, 40 cm square, to be removed were defined. The armature in the motor contained no lead solder, but was constructed with welded connections. The bonding layer underlying the KEL-F coating on our stainless steel SIPRE auger was found to be contaminated with lead. It was stripped and cleaned with acids down to the bare metal. The sides of the blocks were sawn out between the

holes by hand with a teflon-handled non-motorized saw that could be absolutely cleaned and which was especially adapted to make cuts from a blind hole. The blocks were broken loose at the back by driving a stainless steel wedge into a saw cut, and then they were lifted out with a large pair of metal tongs that gripped the block on two opposite sides with spiked pads. The latter were thrust and held by a large, threaded, knurled metal drum driving large diameter screws against the tong arms. Each block was lifted out of place by two men, one holding each arm of the tongs, and lowered into a 120 liter plastic drum, two blocks per drum. The grip of the tong pads could be released by reversing the rotation of the metal driving drum. The polyethylene bags, in which the plastic drums, with lids, were enclosed, were opened just long enough to insert the firm blocks, then they were immediately resealed.

At each level, eight blocks were cut and placed in four drums. The sampling volume was about 75 cm vertical, 150 cm horizontal, and 45 cm front-to-back, except at the virgin site in Greenland, where the vertical dimension was 110 cm, and the horizontal dimension was 75 cm. The sample levels we report are located at the centers of those volumes. The top and bottom planes of the sampling volumes were horizontal, and did not conform to the slopes of the shaft or trench floors. Surface samples were collected at virgin sites and along traverses from trenches dug upwind from all other activities. Shallow upwind surfaces were discarded, and successive layers were separately cut and scooped on the the upwind side with a shovel and dumped into assigned drums. For thin layers, the worker might scoop an area 10 meters long and 2/3 meters wide. Introduction of drifting snow is believed to have been less than one part in twenty in most instances.

Care was taken not to permit nasal mucus to drip onto the blocks.

Wherever the blocks were handled with plastic gloves, or some other form of suspected contamination contact existed, that area was trimmed away with the ice adze when the block was held in the grip of the tongs and while it was being trimmed in an octagonal shape, 38 cm in diameter, to fit the drum just before its insertion. All collection operations, including those at Camp Century and Tuto, were carried out when no other persons except those enclosed in plastic suits were in the shafts, adits, or trenches or their near vicinities. Although about 10 hours were required to sample each level, the drums were open and the final surfaces of the firn blocks were exposed only for a matter of minutes.

In the virgin trench site ESE of Camp Century firn blocks from the upper levels were soft and broke loose from the tong grips. These heavy blocks, especially those from the uppermost level (1963), were unavoidably handled with plastic gloves. We believe that some alkali contamination coming from frozen perspiration may have been introduced into these samples. Considerable amounts of frozen perspiration would sometimes collect on the insides of the plastic suits and gloves and migrate by movement of the limbs to openings, but in most instances this was contained by waist and wrist bands and sleeve guards.

Melting and aliquoting the firn and ice blocks

The polyethylene bagged drums containing the firn block samples were transferred within their sealed wooden boxes from the collection sites to nearby laboratories for melting and aliquoting. The laboratories were wood and canvas Jamesways whose interior floors and lower walls were covered with polyethylene sheeting. The melt-water in the four drums comprising one sample usually totaled about 200 liters. The drum seals were opened, and self-priming polyethylene siphons with stopcocks were inserted into the small opening made by lifting an edge of the lid on each drum, and the water was drained into bottles. During

the transfer, the drum lids were kept on and the bottles were opened only for the few seconds required to fill them. The melt-waters in the four drums were divided among two 50-liter bottles, four 19-liter bottles, and one 8-liter bottle. The water in each drum was measured initially, and then proportioned among all the bottles in the same manner as if the water in all four drums had been first mixed and then poured into the bottles. A few minutes later, 100 ml of 8 N HCl and 15 μ of Pb^{208} tracer were added to two 50-liter and two 19-liter bottles. 100 ml of 8 N HCl was added to one 19-liter bottle.

Cleaning and shipping the containers

The 120-liter polyethylene drums used for melting firn and ice blocks were cylindrical, flat bottomed, and open-topped, and were equipped with flat, friction fitting lids. They were cleaned by forcing them vertically into a 200-liter polyethylene drum partially filled with concentrated reagent grade HNO_3 until all parts, inside and outside, were bathed with acid for a few minutes. They were then rinsed three times with distilled water. They were then rotated horizontally one hundred times in a second large rectangular polyethylene bath containing cold, concentrated reagent grade HNO_3 . They were rinsed four times with water that had been purified with ion exchange resins, double-distilled in silver plated tin, and redistilled in "vycor", using a superheated silicon carbide packed entrainment barrier. That water was stored in polyethylene, although it had passed through a pyrex glass condensing section in the last still. The drums and bath were of such a size as to allow the drums to be taken in and out of a large fume hood, but the drums had to be rinsed outside the hood. The lids were cleaned separately. Workers wore gas masks and polyethylene gloves, which permitted these operations to be carried out in the midst of acid fumes, in a pure-air laboratory which reduced lead contamination

from the air. The cleaned drums were fitted with lids and were immediately placed within polyethylene bags, and filtered argon gas was immediately introduced at such a rate as to displace all the contained air within 10 seconds. The polyethylene bags were then sealed by twisting the opening into a knot and then holding that knot tightly shut with nichrome wire. Previous tests had shown that this seal was effective against half an atmosphere of pressure. Millipore filters in plastic holders had previously been attached to the walls of the polyethylene bags so that pressure changes could be relieved through those filters. The drums and bags were then sealed within outer polyethylene bags that were tight and had no filters. Polyethylene rope handles were attached, and the bagged drums were lowered into individual, sturdy, waterproof plywood boxes. These boxes had been made airtight with epoxy resin, and the lids were screwed down against cork seals with a large number of screws. An electric screwdriver was used to facilitate the opening and closing of the boxes.

Polyethylene bottles used to contain the melted water samples were cleaned, rinsed, filled with argon, and packed in a similar manner. Screw caps were made to give a liquid tight seal by inserting a teflon disk. The water filled bottles were resealed in their polyethylene bags in the field laboratories and shipped back to the United States in their original boxes. A total of 500 drums and bottle boxes, exclusive of other equipment, was shipped to Greenland and the Antarctic, so there was a reasonable probability that a few bottles or drums had been improperly cleaned or had been contaminated during shipment.

ANALYSIS FOR METALS

Isotope dilution (1) lead

In this method a known amount of relatively pure Pb^{208} tracer is mixed with a known amount of acidified melted ice. The unknown amount of Pb^{207} in the ice originating from sea salts, terrestrial dusts, and industrial pollutant aerosols mixes isotopically with the Pb^{208} tracer. This isotopic mixture is chemically isolated by a combination of liquid extraction and ion exchange steps and is then isotopically analyzed in a mass spectrometer. The concentration of Pb^{207} in the sample is determined from the observed ratio $\text{Pb}^{207}_{\text{sample}}/\text{Pb}^{208}_{\text{tracer}}$ the known amount of tracer, and the known amount of sample water.

Our procedure was as follows: 100 ml of 8 N HCl were added at the collection site to the melted ice aliquot which amounted to either 50 kg or 19 kg. 30 μ of Pb^{208} were added, and the sample was agitated. After shipment to the United States and storing, which consumed about 6 months, the pH was adjusted to 7 with concentrated NH_4OH , and 300 ml of CHCl_3 containing 15 mg of dithizone were added. The bottle was clamped in a churn and rotated end over end for 15 minutes, then allowed to stand for 1 hour. The aqueous phase was decanted, and 50 ml of dithizone solution in CHCl_3 which remained was freed of traces of water in a separatory funnel. The CHCl_3 layer was then back-washed with 20 ml of 1 N HCl. The CHCl_3 layer was discarded. The aqueous layer was rinsed with pure CHCl_3 , and 2 μ of nearly pure Pb^{206} tracer were added. The aqueous phase was treated with 2 ml of 25% ammonium citrate, the pH adjusted to 8.5 with concentrated NH_4OH , and 2 ml of 5% KCN were added. This aqueous mixture was extracted with 10 ml of CHCl_3 containing 0.05 mg dithizone/100 ml. The aqueous phase was discarded. The CHCl_3 layer was back-washed with 5 ml of 2 N HCl. The CHCl_3 layer was discarded, and the

aqueous layer was rinsed with pure CHCl_3 . The aqueous layer was loaded on a 5 ml column of Dowex anion exchange resin, Ag 1 - X8 150 mesh, that had been previously washed with 8 N HCl and then with 2 N HCl. After loading, the column was washed with 3 volumes of 2 N HCl, and then stripped with 1.5 volumes of 8 N HCl. The eluate was evaporated to dryness, then evaporated to dryness twice again with a mixture of 8 drops of concentrated HNO_3 and 4 drops of concentrated HClO_4 . The residue was dissolved in 1/2 ml of 2% NH_4NO_3 and then saturated with gaseous H_2S . The PbS ppt was centrifuged, and by means of a micropipette, a portion was transferred to a tantalum filament, evaporated to dryness, and inserted in the mass spectrometer. Lead was analyzed as Pb^+ . A custom-built 12-inch radius, single focusing, thermal emission source mass spectrometer equipped with both electron multiplier and Farady cup collectors was used at the California Institute of Technology, and a similar instrument, constructed by Consolidated Electrodynamics Corporation was used at the University of California at San Diego.

The chemical laboratory was pressurized with filtered air. Evaporations were carried out within glass tanks in an atmosphere of pure nitrogen. Procedures had been planned for blank determinations whereby each sample would be divided into two large and two small aliquots which would be treated in exactly the same manner during analysis. Concentrations could be determined from the slope of the plot of observed amounts of lead vs amounts of sample, while deviations of the points from the curve would give perspective of the error of analysis, and the intercept at zero sample would indicate the blank. Although this method had been satisfactory for most seawater determinations, we found that it would not work well in the case of old, relatively unpolluted polar snows. In this instance, the blank lead was too high relative to the amount of sample lead

present, and differences in yields during the first dithizone extraction step gave rise to erratic results. We therefore abandoned this method and made blank corrections by subtracting off the lead in the reagents. We then considered results from different aliquots of a sample to be multiple determinations, and averaged them.

The step which gave the poorest and most variable was the first extraction of lead into dithizone in CHCl_3 from a very large volume of water that sometimes had small amounts of precipitants beginning to develop at a pH of 7. We monitored this yield for each aliquot in every sample with Pb^{206} tracers, reading the yield from the observed $\text{Pb}_{1\text{st}}^{208} / \text{Pb}_{2\text{nd}}^{206}$ ratio. These yields varied from 95% to 45% and averaged 80%. The known amount of reagent lead blank from the HCl , NH_4OH and CHCl_3 added previous to this step plus unknown amount of sample lead was then corrected for this yield before calculating the effects of lead contamination added after the first extraction. The combined yield for all succeeding analytical steps up to and including the ion exchange column was greater than 95%, as shown by previous tests with tracers. We therefore made no yield corrections for known reagent and air exposure lead blanks subsequent to the first solvent extraction step.

The lead blank obtained from the standard invariant procedure subsequent to the first dithizone extraction step was determined by isotope dilution, and was $0.07 \gamma \text{ Pb/run}$. The concentrations of lead in large volumes of NH_4OH , HCl , and CHCl_3 were determined by isotope dilution, using the method outlined above for seawater, and these values ($0.0003 \gamma \text{ Pb/ml NH}_4\text{OH}$, $0.0004 \gamma \text{ Pb/ml undistilled HCl}$, $0.00005 \gamma \text{ Pb/ml of distilled CHCl}_3$), were also used in making blank corrections for the procedure previous to the first dithizone extraction step.

All reagents except CHCl_3 were prepared with teflon, polyethylene, or quartz containers and tubing only, and were stored in polyethylene. "Tygon" tubing was avoided. HCl was prepared from filtered, compressed gas and pure water. Some of it was further purified by vacuum distillation in quartz. HNO_3 and HClO_4 were purified by vacuum double distillation of reagent grade materials in quartz. Both these acids were stored in pyrex. The cyanide and citrate solutions were purified by repeated dithizone extractions at a pH of 8, followed by readjustment of the cyanide solution pH with concentrated NH_4OH . NH_4OH was prepared from filtered, compressed gas and pure water. CHCl_3 was double distilled in pyrex starting with the commercial, especially purified lead-free reagent material.

Pyrex separatory funnels with unground glass surfaces equipped with teflon stopcocks and stoppers were used. Pyrex beakers and centrifuge tubes were used. Green and white lead glaze trade names and decorations were either missing or had been ground off. All glassware had been boiled in concentrated HNO_3 , rinsed with the purified water mentioned earlier in the bottle cleaning section, handled with stainless steel tongs, and wrapped in "Saran" film.

Multiple determinations of a sample scattered less as the absolute concentration of lead increased in the sample. As shown in Table 1, scatter about the mean changed typically from 75% at 0.004 γ Pb/kg to 2% at 0.207 γ Pb/kg.

(Please insert Table 1 here .)

This shows that variability in blanks is a principal source of error when the amount of lead in the sample becomes small, but there is evidence that other factors operate to cause large error. As shown by the example in Table 2, unusually large variations in concentrations were observed, and these cannot

Table 1. Scatter of measured lead concentrations

Sample	Successive observed lead concentrations in different aliquots of a sample (γ Pb/kg)				Mean	Limit of scatter from mean
65-26	0.007	0.001	0.004	--	0.004	75%
65-25	0.017	0.010	0.011	0.019	0.014	35%
65-5	0.040	0.047	0.040	0.032	0.039	20%
65-18	0.140	0.132	0.150	0.148	0.142	8%
65-23	0.203	0.210	0.207	0.210	0.207	2%

be related to uncertainties in blanks already considered.

(Please insert Table 2 here.)

We believe that there are two likely causes of this aberrant effect. Occasionally there may be large, spurious clots of lead contamination partially buried in the walls of some of the polyethylene bottles. Partially exposed fragments of foreign material embedded in the cleaned containers could be seen under the microscope. Occasionally a few large clots of undissolved lead material may exist in the melted ice which cannot be proportioned well by aliquoting. In some instances we have discarded a result if it was more than a factor of two out of line, because it must have originated from some unavoids, spurious contamination, but we could not ignore moderately high values such as those listed in Table 2 and had to include them in the averages. In some instances we did not obtain results at all because the techniques were carried out improperly.

There were small and variable amounts of lead added to the samples from the walls of the drums and bottles which were not included in the blank corrections mentioned above, but which we believe can be estimated as the average excess lead found in the 800 BC Greenland sample and found in the samples older than 1775 AD in the Antarctic in excess of that which should have been supplied by natural sea salts and terrestrial dusts present in those samples. This correction averaged about 0.06 γ of lead per 19 to 50 kg of sample water, and it originated from both a 120-liter melting drum and a 19 or 50-liter sample bottle to which the sample water had been exposed. This correction appears to be justified because these samples are too old to have been affected by atmospheric lead pollution on a scale that could be measured by these techniques.

It is likely that this residual blank of 0.06 γ of lead originated from container walls and not from contaminated air. Outside air was about ten times

Table 2. Scatter of measured lead concentrations

Sample	Successive observed lead concentrations in different aliquots (γ Pb/kg)				Mean	High/low
65-15	0.347	0.544	0.378	--	0.423	1.57
65-19	0.077	0.074	0.076	0.121	0.087	1.64

higher than laboratory air, which probably averaged $0.5 \text{ } \gamma \text{ Pb/m}^3$. Lead in laboratory air originated from that entrained on shoes. A melting drum could have contained $0.05 \text{ } \gamma \text{ Pb}$ dispersed in its air after cleaning, but most of this lead should have been expelled when the drum was filled with pure argon.

We believe that isotopic equilibration was achieved between the lead tracer and most lead present in each of the acidified melted ice samples because the lead originated mainly from readily soluble industrial pollutant aerosols. The concentration of sea salt sodium averaged about $20 \text{ } \gamma \text{ Na/kg}$ snow within the interior of Greenland. The ratio of lead to sodium in sea salts is of the order of 5×10^{-9} (CHOW and PATTERSON, 1962), so the amount of sea salt lead in the snows was about $10^{-7} \text{ } \gamma \text{ Pb/kg}$ snow. The concentration of non-sea salt potassium averaged about $2 \text{ } \gamma \text{ K/kg}$ snow within the interior of Greenland. The ratio of lead to potassium in terrestrial dusts is of the order of 4×10^{-4} (CHOW and PATTERSON, 1962), so the amount of terrestrial dust lead in the snows was about $8 \times 10^{-4} \text{ } \gamma \text{ Pb/kg}$ snow. The lowest lead concentration assigned to a sample was $0.004 \text{ } \gamma \text{ Pb/kg}$, while all others were above $0.014 \text{ } \gamma \text{ Pb/kg}$. Therefore all but an undetectable trace of the lead probably originated from industrial sources. Lead contamination from the polyethylene drums and bottles is acid soluble and is readily homogenized with the lead tracers. Lead aerosols from smelter fume and automobile exhausts are also readily soluble in acids and should have also equilibrated with the lead tracer during the months-long storage period.

There was concern whether polyethylene cleaned with HNO_3 would absorb the more labile lead tracer before it could mix with the less labile pollutant lead. A number of experiments were carried out to check the degree of lead absorption by polyethylene cleaned with HNO_3 . Identical amounts of Pb^{208} tracer were added to separate large carboys cleaned in the regular manner

containing, respectively, 19 liters of pure water, 0.02 N HCl, 0.02 N NH_4Cl , and then this lead was extracted immediately from one set of carboys and several months later from a duplicate set of carboys. The amounts obtained were checked in all cases with a fixed amount of Pb^{206} tracer added just before withdrawal. The ratios of Pb^{208} to Pb^{206} tracer were the same in all instances, showing that no lead was absorbed by the polyethylene under these conditions.

Isotope dilution (2) (3) calcium and potassium

Calcium and potassium were determined simultaneously in a single aliquot of a sample by isotope dilution using Ca^{44} and K^{41} enriched tracers. Our procedure was as follows. One γ of Ca^{44} spike in 0.1 gram of 5% HNO_3 and 0.1 γ of K^{41} spike in 0.1 gram of 5% HNO_3 were weighed out in a 30 ml clear teflon beaker. The 19-liter sample bottle was agitated and 20 grams were poured directly from it into the teflon beaker and weighed. The mixture was evaporated to 20 microliters in a heated, platinum bottomed, teflon tank which had filtered, high-purity nitrogen gas streaming through it. The small, strongly acid drop of liquid was transferred to a tantalum filament by means of a quartz micropipette. The drop was slowly evaporated to dryness and the filament was inserted into the mass spectrometer. Potassium was analyzed as K^+ , calcium as Ca^+ .

All containers were of teflon, polyethylene, and quartz, and were cleaned in hot, concentrated pure HNO_3 and rinsed with our purest water. This water contained about 1 γ K/kg and 5 γ Ca/kg, which approximated the concentration of potassium and calcium in the samples. Investigators handled all equipment with stainless steel tongs and wore polyethylene gloves.

Contamination of the samples by potassium and calcium from polyethylene carboys or absorption of metals from sample waters by plastic walls were checked by comparing the concentration of these metals in aliquots of a sample that had

been stored in 8-liter and 19-liter polyethylene bottles. The ratio of polyethylene surface area to sample volume was about 30% higher for the smaller aliquots. As shown in Table 3, no difference was observed for the greater exposure to polyethylene in the smaller bottle after a storage of about 16 months.

(Please insert Table 3 here.)

There was concern as to whether the potassium and calcium in the dust particles in the melted ice samples mixed with the potassium and calcium in the tracers. If it did not, our results would tend to be low, since the tracer metals in a salt matrix would tend to be driven off from a heated filament in the mass spectrometer more easily than metals bound up in a silicate matrix. However, we usually saw no change with increase in temperature which meant that equilibration between sample and tracer was complete.

Considerable amounts of silicate dusts, and even quartz will dissolve in water under equilibrium conditions. 140,000 γ of SiO_2 are soluble as monosilicic acid in 1 kg of water in the pH range of 1 to 8 at room temperature (ALEXANDER et al., 1954). About 400 γ of potassium are present in one kg of a saturated solution of microcline in water at room temperature and a pH of 7. The amount of potassium increases to about 40,000 γ K/kg when the pH is lowered to 2 (FETH et al., 1965). But we are concerned with rates of dissolution, not ultimate solubility. For example, STOBBER (1967) claims he could not observe the dissolution of monosilicic acid from suspensions of finely divided vitreous silica in neutral water in amounts greater than 500 γ SiO_2 /kg of water after several weeks. The limit of sensitivity of his method was 500 γ SiO_2 /kg water. ALEXANDER et al. (1954), found that under similar conditions the concentrations of dissolved monomeric silica increased to a constant within three weeks. In the latter case the pH was 5.6. All of the above work does not consider polymerized

Table 3. Replicate analyses of sample 65-3 stored for 16 months in different polyethylene containers at pH of 7

	8-liter bottle	19-liter bottle
γ K/kg snow	2.6 , 2.2	2.2 , 2.4
γ Ca/kg snow	7.1 , 6.9	6.8 , 7.9

silica in solution. MOREY et al. (1964), found silicon reached levels of 1500 γ SiO_2 /kg water after about 14 days, starting with powdered silica glass and pure water in polyethylene bottles and after about 30 days, starting with powdered crystalline quartz and pure water. These concentrations were rather unreliable, but they had risen to values of 129,000 γ SiO_2 /kg water for powdered silica glass and 60,000 γ SiO_2 /kg water for powdered crystalline quartz at the end of one year.

The probabilities of dissolving finely divided dusts, or at least leaching alkalis and alkaline earths out of them, should be very great if the dusts are stored at a high dilution and at a pH of 2 for 16 months, yet we could observe no difference between concentrations of potassium and calcium in acidified and in non-acidified 19-liter aliquots of the same sample that had been stored for long times. This is shown in Table 4.

(Please insert Table 4 here.)

This suggests that practically all of the potassium and calcium in the silicate dusts in the snows may either be leached out by the melted waters after more than a year of standing or else approximate isotopic equilibration between potassium and calcium in the tracers and in the dusts may be achieved when the waters are concentrated into drops of hot, strong acid during the process of evaporating to dryness, and during the higher temperature heating on the filament in a minute, molten, corrosive flux of sea salt sodium chloride.

It should be recognized that neither the bulk of the potassium nor the calcium in the snow from the interior of Greenland originates from readily soluble sea salts. On the contrary, about 80% of the potassium and 90% of the calcium found within such snows cannot be assigned to sea salts, according to the sodium and chlorine concentrations in them,

Table 4. Replicate analyses of sample 65-19 stored for 16 months
in 19-liter polyethylene carboys at different acidities

	pH = 2	pH = 7
γ K/kg snow	5.0, 5.0	4.5, 4.9
γ Ca/kg snow	6.1, 6.0	5.8, 6.0

because the concentrations of the latter elements are too low. It should also be recognized that we do not find an excess of silicon or titanium in these waters to go with the non-sea salt potassium and calcium that is found. On the contrary, total silicon determined by emission spectrography is so low relative to these metals, that one must assume they originate from mixtures of limestone dusts and potash-rich illite clays. There is no reason for believing, therefore, that there are analytical deficiencies of potassium and calcium which result from incomplete dissolution of silicate dusts. It seems likely that the potassium and calcium concentrations measured by this method reflect the total amounts of both metals, dissolved and suspended, in the water.

Isotope dilution (4) titanium

Titanium was determined by isotope dilution using a Ti^{48} enriched tracer. Our procedure was as follows. 0.5 μ of Ti^{48} tracer in 0.05 gm of 5% HNO_3 was weighed in a 100 ml clear teflon beaker. 90 grams of sample were added to this beaker and weighed. The sample was decanted directly from the 19-liter carboy after it had been agitated. The mixture was evaporated to dryness in a teflon tank kept free of dust and condensed water by a flow of filtered nitrogen. The small spot of residue in the beaker was dissolved in one drop of concentrated HNO_3 , and again evaporated to dryness. The residue was transferred as a slurry in one drop of water to a tantalum filament with a quartz micropipette and again evaporated to dryness, and then baked slightly. Titanium was analyzed in the mass spectrometer as TiO^+ . The tantalum filament had been outgassed at high temperature in a vacuum and then flashed in air to coat its surface with a thin film of oxide before the sample was evaporated on it. The analysis was repeated for each sample until at least two satisfactory analyses were obtained.

Equipment cleaning procedures, handling, and laboratory conditions were

the same as outlined in the methods for lead, potassium, and calcium. The titanium blank was incorporated into the tracer by using its isotopic composition determined under standard conditions of analysis in the absence of a sample. The concentration of titanium in our purest water was less than 0.002 γ Ti/kg.

It was more difficult to obtain constant Ti^{48}/Ti^{49} ratios during a mass spectrometric run than had been the case for potassium and calcium, probably because it was more difficult to achieve isotopic mixing between titanium in the tracer and in the sample. When changing ratios were observed, the Ti^{48}/Ti^{49} ratio usually decreased with increasing temperature. This suggests that the Ti^{48} tracer was more mobile than the sample Ti^{49} located within a silica matrix. Changing ratios could usually be avoided by adding HNO_3 to the mixed residue of evaporated sample and tracer and evaporating again to dryness.

HF was used as a more drastic method of equilibrating tracer and sample. In this procedure, the sample and tracer mixture was evaporated to less than 1 ml, three drops of concentrated HF were added, and the evaporation continued to about 20 microliters. Several drops of concentrated HNO_3 were then added and the evaporation was continued to a moist paste. Concentrated HNO_3 was again added and evaporated to dryness. The residue was transferred as a water slurry to the filament. As shown in Table 5, more titanium could be obtained from samples subjected to the HF treatment. We did not use it routinely because the volatility of titanium fluoride made the procedure unreliable. The HF treatment analyses reported in Table 5 are selected.

We also compared titanium concentrations in acidified and non-acidified aliquots of water that had aged for 18 months. As shown in Table 5, more titanium could be obtained from samples subjected to prolonged acid treatment. We did not routinely analyze the acidified aliquots because small amounts of polyethylene had dissolved in these acidified waters and this material resisted

degradation and rendered the analysis difficult and unreliable. The analysis of acidified water reported in Table 5 has been selected. No difference was observed between the titanium concentration in samples taken from a carboy before and after it had been agitated.

(Please insert Table 5 here.)

Our titanium results may also be low because some of the dust particles may have been removed from the melted ice while it was standing in the melting drums. It was observed that rings of dark, amorphous material about one centimeter wide had formed on the interior drum walls at the waterline of some of the drums. The rings could be seen after the water had been siphoned away. A record was kept of the intensity of the rings after this phenomenon was noticed. The rings do not appear in melted ice older than 1908 from the interior of Greenland, and they do not appear in melted ice older than 1952 from the vicinity of New Byrd Station in Antarctica. The intensity of the rings varied widely. No rings could be observed in any of the drums for a few age levels above 1933 in Greenland and above 1952 in Antarctica, while some drums at a given age level would show strong rings and others would show weak, or no rings at all. It should be recognized that different firn blocks sometimes represented different seasons.

Although the rings contain some visible microscopic particles, they are believed to consist mainly of a carbonaceous film which at first floated on the surface of the water as a minute scum, and which then migrated to the drum walls and adhered there. This material probably originates from carbonaceous fuels, but it is not known whether the fuels were petroleum or coal, or whether they were locally derived.

Our concern with these rings is that the oily film may have scavenged

Table 5. Replicate analyses for titanium (γ Ti/kg snow)

Sample	Stored at pH 7 for 18 months. Evaporated with HNO_3 .	Stored at pH 7 for 18 months. Evaporated with HF .	Stored at pH 2 for 18 months. Evaporated with HNO_3 .
65-22	0.038	0.048	0.057
65-25	0.038 , 0.075 0.042 , 0.042	0.055 , 0.079	-

dust particles out of the melted ice water before it was aliquoted into the carboys. There is some evidence that this did happen. The average uncorrected titanium concentration in Greenland snows which did not yield carbonaceous rings is 0.045 γ Ti/kg, while that for snows which did yield rings is only 0.028 γ Ti/kg. Furthermore, one of the rings had been sectioned out of a drum and brought back to the U.S., and a segment of this ring was leached with HF and that solution was analyzed for titanium. The total ring contained approximately 0.8 γ of titanium and it came from a drum that had held about 50 liters of melted snow. That volume of melted snow contained, after being siphoned from the drum, about 1.4 γ of titanium. The oily film may have scavenged some of the titanium in dust particles out of the melt-water. We do not believe that amounts of lead, potassium, or calcium in the rings were appreciable compared to the amounts present in the siphoned melt-water, however.

Isotope dilution (5) magnesium

A check was made on a few samples for total magnesium, using isotope dilution of enriched Mg^{26} . 90 ml of sample were evaporated to dryness with 45 γ of magnesium tracer in a nitrogen atmosphere teflon tank. The residue was acidified with HNO_3 , evaporated to dryness again, and loaded with a solution containing 20 γ of H_3BO_3 on a rhenium filament. There was no evidence suggesting that the tracer did not equilibrate with the magnesium in the sample. The method was not used to check all samples because it was unusually time consuming.

Neutron activation (1) chlorine

Chlorine was determined by neutron activation. Upon irradiation by neutrons, 37 minute Cl^{38} was formed in the water, and its activity was compared with that of a standard irradiated at the same time. Our procedure was as follows.

11 grams of water were poured out of the 19-liter carboy into a 4-dram snap-top polyethylene vial. The vial was welded shut with a soldering iron and sealed in a polyethylene bag. It was irradiated 30 minutes in a flux of 1.8×10^{12} thermal neutrons $\text{cm}^{-2} \text{sec}^{-1}$. The vial was removed from the bag, washed, and 80 milligrams of 2 N NaOH were injected by means of a hypodermic needle. The hole made when the needle was withdrawn was sealed with a finger and the vial was shaken vigorously for 10 seconds. The top of the vial was cut off and air was aspirated through the liquid for 20 seconds to remove radioactive argon. The liquid was poured into a new weighed vial so that the radioactive vial could be discarded. Each sample was immediately counted over the entire spectrum from 0 - 3 Mev for 10 minutes and then for two more 10 minute periods at 30 minute intervals. The 1.6 Mev peak of Cl^{38} was used for the determination. A chlorine standard solution, treated in exactly the same manner, was also counted. The samples were weighed after counting. The composition of the samples was such as to give relatively clean Cl^{38} peaks. Mn^{56} , $\text{K}^{40,42}$, and, in most cases, Al^{28} , did not interfere. In several samples, Al^{28} was observed in the initial count. In these samples, the first count was discarded, and by the time the samples were recounted, the 2.3 min Al^{28} had decayed. Observed decays of the 1.6 Mev peak adhered closely to a 37 minute half-life during the 10 to 80 minute period after irradiation. Ar^{41} was the major source of interference at the beginning of the counting period and Na^{24} was the major source of interference near the end of the counting period. Total first counts on peaks ranged from 1000 to 2000. Counting errors amounted to about 4%. All reported chlorine determinations were made in duplicate on the original ice melt-waters without any chemical separations. The standard was about one hundred times more concentrated than the samples.

There were 840 γ Cl/kg of polyethylene vial, and a net amount of Cl^{38} equivalent to 0.03 γ of chlorine contamination was added to each 11 gram water sample irradiated for 30 minutes in a 4-dram polyethylene vial. Most irradiated samples contained 0.8 to 0.4 γ of Cl.

Serious contamination came from the polyethylene carboys during the 24 months storage period. The chlorine content of several samples stored in large and small polyethylene containers was compared, and, unlike the data obtained for metals, there was a positive contamination effect which could be verified by duplicates. Some ice from each sample had been collected and stored in pyrex bottles, however. This water contained about 10% less chlorine than water stored in 19-liter polyethylene carboys. The contamination correction was estimated to be 100 γ of chlorine per 19-liter carboy.

It is believed that an effect was found to exist between the observed cpm/ γ Cl and the amount of chlorine irradiated, when the amounts varied by a factor of a hundred, although errors are so large as to make it doubtful. Because this effect appears consistent with our observations on spiked samples, we have applied a further negative correction of 5% to all our results, in addition to the correction for 0.03 γ of chlorine contamination by the polyethylene vials and the 100 γ Cl/19-liter carboy contamination.

Neutron activation (2) sodium

Water samples were irradiated in a neutron flux, and the activity of the 15 hr Na^{24} formed was measured and compared with the activity of a standard irradiated at the same time. In our procedure sodium was counted later in the same samples that had first been counted for chlorine. Additional steps for sodium were as follows. Both the samples and standard were counted over the entire spectrum from 0 - 3 Mev about 16 hours after irradiation, when most

short-lived nuclides had decayed away, and the spectra were relatively clean. The 2.75 Mev peak of sodium was used in the determination. The decay rate was checked by an additional count 12 hours later. The composition of the sample waters was such as to give clean sodium peaks, and no interference was suspected. Observed decays adhered closely to 15 hours. Total first counts on peaks were about 3000. Counting errors amounted to about 3%. All sodium determinations were made in duplicate on the original ice melt-waters without any chemical separations.

The concentration of sodium in the polyethylene vials was 810 γ Na/kg, and Na²⁴ equivalent to 0.006 γ of sodium contamination was added to each 11 gram water sample in a 4-dram polyethylene vial during a 30 minute irradiation. The amounts of sodium in the sample waters ranged from about 0.2 to 0.4 micrograms.

Waters stored in pyrex were grossly contaminated with sodium. A sample containing 15 γ Na/kg when stored in polyethylene was found to contain 65 γ Na/kg when stored in pyrex. We measured sodium in two different samples that had both been stored in 19-liter polyethylene carboys and in 4 and 8-liter polyethylene bottles, but could find no difference, though there was a 30% difference in the area of polyethylene exposed to the liquids. This is shown in Table 6. It appears that either negligible sodium contamination originated from the polyethylene containers, or else adsorption of dissolved sodium on the plastic container walls was balanced by sodium contamination. No corrections were made for sodium contamination by the polyethylene containers.

(Please insert Table 6 here.)

Atomic absorption (1) sodium

Sodium was determined by partially freezing the samples into large amounts of ice and small amounts of concentrated brines, and then atomizing these brines directly into the flame of the atomic absorption spectrophotometer. The absorption intensities

Table 6. γ Na/kg snow

Sample	4-liter polyethylene bottle	19-liter polyethylene bottle
65-14	9.6 , 8.5	9.3 , 9.7
65-26	340	330, 350, 350, 350

of the samples were compared with those of standard solutions. Except for pouring into cleaned polyethylene bottles, the samples were not otherwise exposed to contamination by processing. This procedure was considered superior to a freeze-drying method for concentrating our samples because the latter method is subject to more contamination problems at the concentration levels encountered in polar snows. Containers must be reused and re-cleaned. Seals moving against each other tend to be abraded. Pump fumes must be trapped before they enter the system, yet such a trap must have a capacity of many kilograms of water.

Our procedure was as follows. 3.5 kilograms of weighed sample were chilled at about -15°C in a plastic bottle so that 90% of it was frozen after 7 days. The bottle was encased in two loosely fitting, but tightly sealed plastic bags. Ice forming on the sides of the bottle was broken loose and the contents were violently shaken four times a day during the freezing period to inhibit the formation of trapped pockets of brine. The final liquid was decanted into a small polyethylene bottle and weighed. The ice residue was remelted and frozen again in the same manner as before, and a second liquid fraction formed after 7 days was decanted and weighed. The ice residue was remelted and frozen again, and a third liquid fraction was decanted and weighed. Each liquid fraction was analyzed separately and in duplicate in the atomic absorption unit by pouring some of the contents of its bottle into its cap and inserting the intake tube of the aspirator into the liquid in the cap.

We used a Nippon Jarrel Ash Model 1 instrument equipped with Westinghouse ion tubes, a hydrogen, compressed-air, burner-atomizer, and a multi-pass system. Our photo-detector was of the broad range, medium sensitivity type. Gas pressures were adjusted to give maximum intensity commensurate with minimum instability and response to pressure changes.

Standards were made with sodium salts dissolved in melted ice that had been frozen from our purest water. Our blank was that same melted ice water, and its absorption was subtracted from those observed both in the standards and in the samples. The concentrations of sodium in our purest water was about the same as those in the samples, and ice frozen from this water still contained appreciable amounts of metal. The light scattering effect of water vapor was greater than the absorption caused by residual traces of sodium in the solvent used to make up the standard. The amounts of metal found in the three brines were summed, with appropriate adjustments for volume changes, to obtain the total concentration of metal in the original sample.

This method worked best for sodium in our samples because sea salt sodium was the major metal in polar snows, and it was efficiently concentrated in the brines by freezing. Sodium was concentrated to about 150 γ /kg in the first brines, to about 50 γ /kg in the second brines, and to about 20 γ /kg in the third brines. Sodium could be determined quantitatively in all but 5% of the third brine concentrates.

The partial freezing method gave low results because not all the metals are confined to the first brine concentrate, and some of the remainder cannot be detected. Silica gels may be quite effective in withholding some metals from the brine phase and trapping them in the ice phase. Our observations are not in accord with those of SMITH and TASKER (1965) who reported more efficient concentration factors for solutions that were continuously agitated. Their solutions were frozen much more rapidly than ours, however.

In the three coastal glacier samples, the concentrations of sodium were too high for analytical conditions suitable for the other samples, BEER'S law was not

obeyed, and the results were low. With these exceptions, measurement errors for the total observed concentrations of sodium in the polar snows were about the same as measurement errors of sodium determined by neutron activation. A correction factor of 1.1 was obtained from the slope of the regression between atomic absorption and neutron activation determination of sodium, and all atomic absorption values were increased by this factor to account for loss during freeze concentration. The regression is shown in Figure 1. Atomic absorption measurements were low by a small constant, $1 \text{ } \mu\text{Na/kg}$, which may be related to the blank correction. The loss of sodium into the last ice phase was checked in one sample by neutron activation, and it was found to be 14% of the total in the sample.

(Please insert Figure 1 here.)

Atomic absorption (2) magnesium

This method was quite sensitive for magnesium. Even though its concentrations were much less than those of sodium, it could still be measured quantitatively in 65% of the third brine concentrates. Magnesium was about $20 \text{ } \mu\text{/kg}$ in the first brine, about $15 \text{ } \mu\text{/kg}$ in the second brine, and about $5 \text{ } \mu\text{/kg}$ in the third brine.

It is believed that considerable amounts of magnesium were retained in silica gels in the ice phases and were lost to the brines, so a check was made on several samples for total magnesium, using isotope dilution. Analyses for magnesium by isotope dilution and by atomic absorption are compared in Figure 2, where it can be seen that concentration by freezing resulted in a 35% loss of magnesium in the ice. We used a correction factor of 1.6 to increase all concentrations determined by atomic absorption.

(Please insert Figure 2 here.)

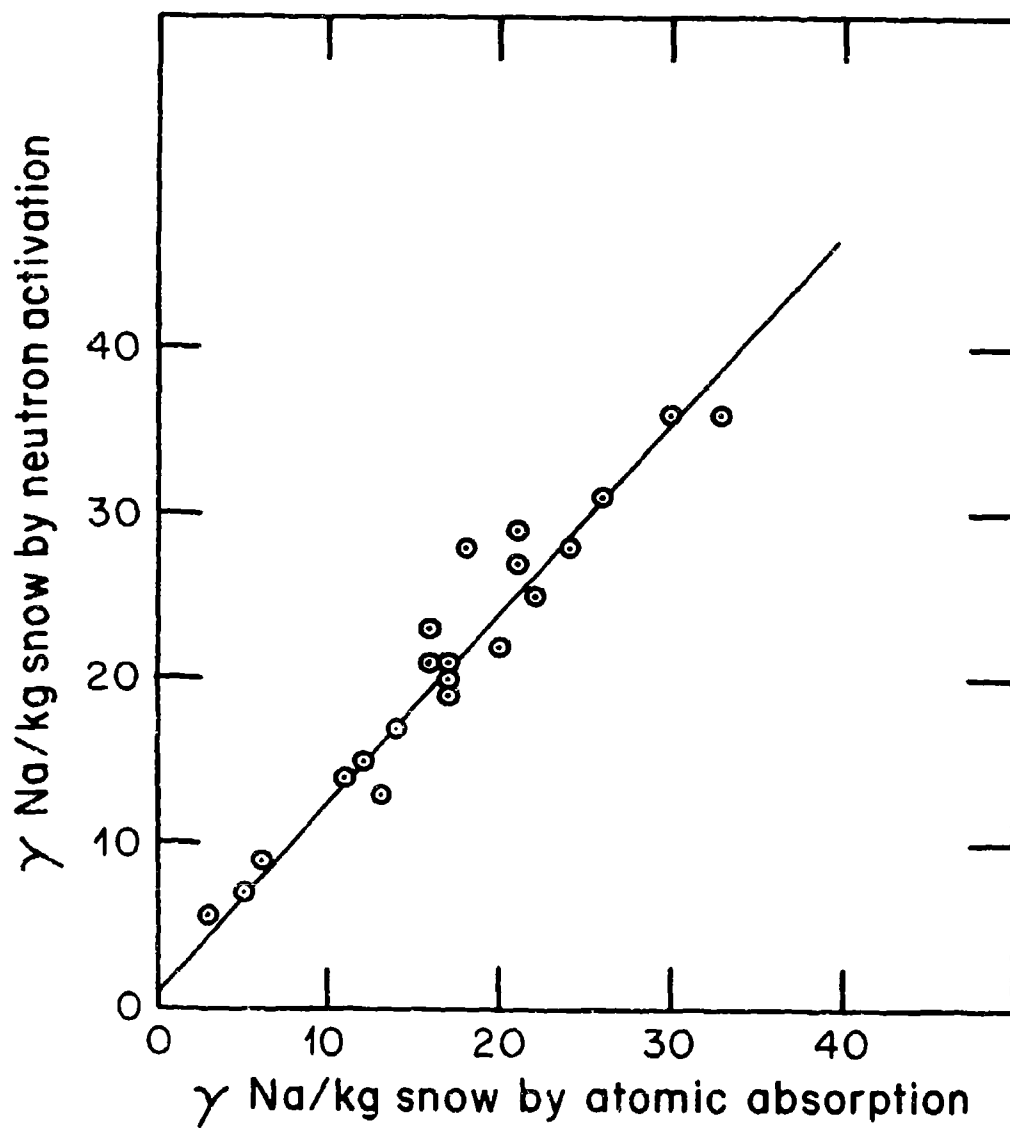


Figure 1: Comparison of sodium analyses of Camp Century and New Byrd Station snows by two different methods.

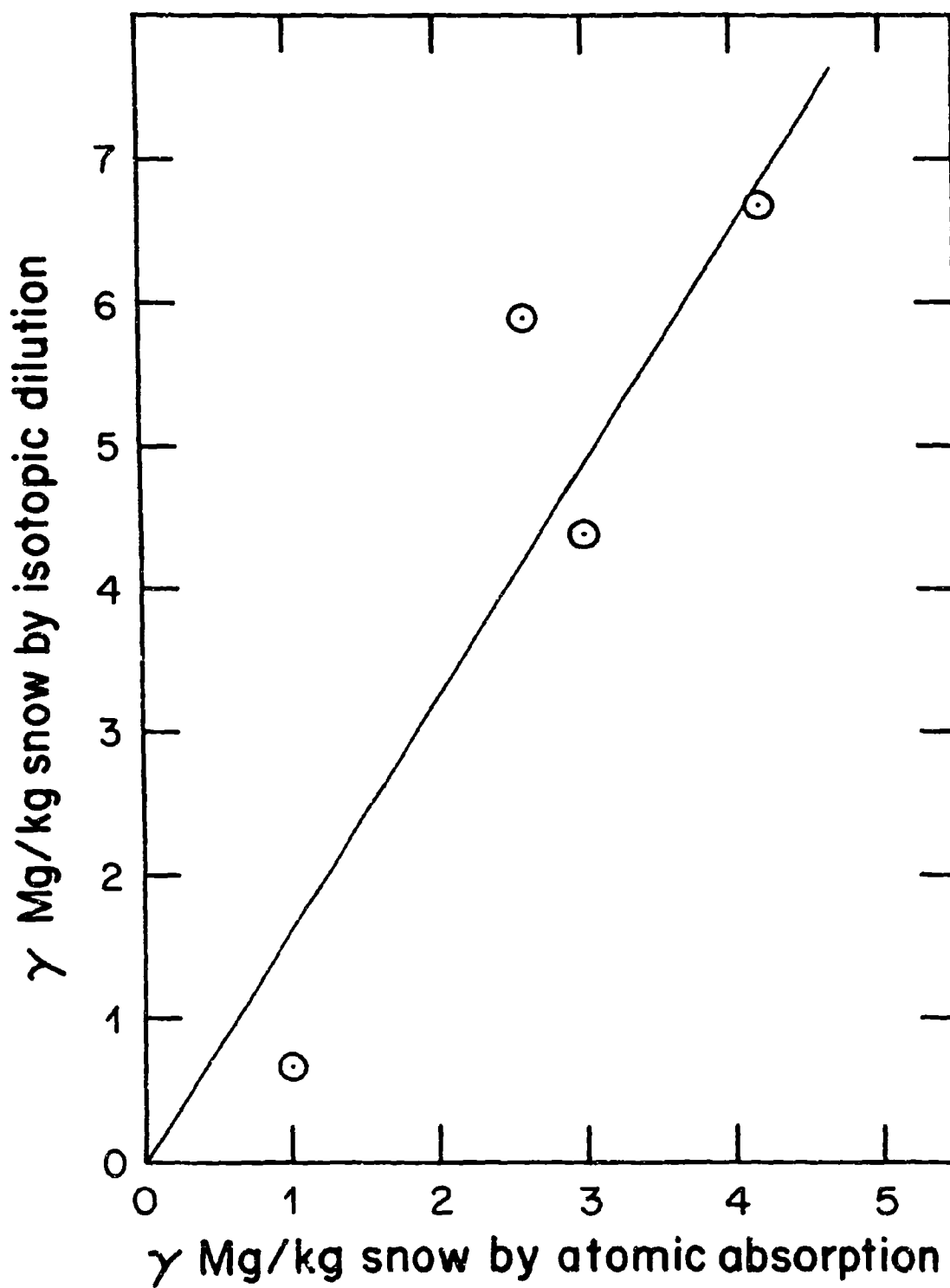


Figure 2: Comparison of magnesium analyses of Camp Century snows by two different methods. Principal difference is due to loss of magnesium during freeze concentration.

Atomic absorption (3) (4) potassium and calcium

Potassium was more sensitive than calcium. Nevertheless, potassium could no longer be detected in the second brine concentrates of half the samples, when concentrations dropped below about 5 γ K/kg in the solution being fed into the aspirator. In the first brines, concentrations were about 15 γ K/kg, and it appears that a little more than half of the detectable potassium in the samples was retained in the first brine concentrates. Potassium could not be detected in the third brine concentrates.

The concentrations of potassium measured by atomic absorption gave a good regression when compared with results obtained by isotope dilution. This suggests that the atomic absorption method, even at these limiting concentrations, is useful. The slope of the regression clearly indicated, however, that the atomic absorption potassium results are quite low relative to the isotope dilution results. We believe that the difference is due to the retention of potassium in the ice phase during the preparation of the samples for analysis. Because of the borderline sensitivity of the atomic absorption method in our situation, we did not use the atomic absorption potassium results in the tabulation of final results, although they lent reassurance and guidance to our isotope dilution determinations of potassium.

Quantitative results for calcium determined by atomic absorption were not tabulated in the final results because the sensitivity was too low. On a semi-quantitative basis the results agreed with those obtained by isotope dilution, however, and it can be said that quantitative results by atomic absorption seem possible for concentrations only a little greater than 60 γ Ca/kg in the solution being fed into the aspirator.

Emission spectrographic analysis for silicon

Total silicon in polar ice was measured by adding a small amount of salt to the water, evaporating to dryness, and arcing the salt in the source of an emission spectrograph (WILSON, 1953). The intensity of the silicon line was compared with those obtained from a series of silicon standards in salt. Our procedure was as follows. 30 milligrams of NaCl and 30 milligrams of Na_2CO_3 were added to 400 ml of sample in a shallow teflon beaker. The liquid was partially evaporated and additional sample was added and the evaporation continued. More sample was added repeatedly until about 3 kg had been evaporated. 0.2 milligram NaF was added to the final aliquot of water. The salt residue which formed upon complete evaporation was scraped out and 15 mg samples were weighed into hollow graphite electrodes and burned completely in a dc arc. Standards exposed on the same photographic plate had been previously prepared by evaporating small amounts of standard NaCl and Na_2CO_3 solutions containing varying amounts of Na_2SiF_6 .

Electrostatic charges seriously interfered with the removal of salts from the teflon beakers. This problem was solved by placing a number of radon therapy needles on the end of a plastic stick, and exposing the interior of the beaker to radiation from the needles before the salts were removed. After several movements of stainless steel spatulas against the salts within the beaker, it was necessary to repeat the exposure process.

About 30 hours of continuous evaporation were required to prepare each sample for analysis. Evaporations were carried out in shallow teflon beakers enclosed by clean, close-fitting massive aluminum blocks which rested in turn upon hotplates completely sealed in clean stainless steel shells. These furnaces

were placed upon a stainless steel bench beneath a thick plastic canopy that was open on all sides. The laboratory floors, walls, and ceiling were coated with plastic. It was hermetically sealed and pressurized with air which had been passed through ultra-filters. Benches were wiped and floors were hosed down before each evaporation. Beakers were cleaned by soaking in concentrated solutions of hot reagent grade Na_2CO_3 , rinsed, soaked in ultra-pure NH_4OH , and then rinsed with portions of the water being analyzed.

We tried strontium as a trace and molybdenum as a macro internal standard, but were unable to solve segregation problems during final evaporations and did not use an internal standard. We chose a mixture of NaCl and Na_2CO_3 that, when dissolved, gave a solution whose pH was high enough to keep all HSiO_3^- in monomeric form. We then added a soluble, gravimetric form of silicon to the standards and a small amount of NaF to the samples.

Air contamination blanks, obtained by exposing small quantities of the NaCl - Na_2CO_3 salt solution in unheated beaker assemblies for 30 hours, were verified by contrasting analyses of Camp Century and Byrd Station ices, which were found to differ in silicon content by a factor of ten. Blank corrections amounted to about 5% in the former samples and about 50% in the latter.

We assumed that silicon contamination from the polyethylene carboys containing the samples was negligible. On this basis, we measured the extent of silicon adsorption onto container walls from sample waters by leaching the carboys (after the contents had been analyzed) with small quantities of concentrated ultra-pure NH_4OH , and analyzing the leach solution for silicon. The amounts found, minus the silicon originally in the NH_4OH , were added to the total solutions originally in the carboys. This positive correction was 30% for both the Byrd Station ices and for the Camp Century ices.

Silicon concentrations are reported in four representative snow samples, but they are the product of a number of preliminary analyses on other snow samples. Two to four evaporations were carried out for each of the representative samples, providing two to four salt deposits for each sample. Two portions of each salt deposit were arced on two different days on separate plates. A set of standards was arced for each plate, and each plate was separately calibrated. Silicon intensities were determined at two frequencies from two separate working curves on each plate.

Colorimetric analysis for chloride

We determined chloride in polar snows by measuring the intensity of a $\text{Fe}(\text{SCN})_2^+$ complex formed when Cl^- was added to $\text{Hg}(\text{SCN})_2$ and Fe^{+3} . Our samples were concentrated by the freeze concentration method described earlier. Our colorimetric procedure was as follows. 50 ml of the brine concentrate were shaken with 15 ml of 0.15% $\text{Hg}(\text{SCN})_2$ in 60% dioxane and 40% absolute ethanol, and with 10 ml of 5% $\text{Fe}_2(\text{SO}_4)_3$ in water in a stoppered erlenmeyer flask. The reagents and sample were brought to 15°C before mixing and kept at that temperature for 30 minutes in a dark room after mixing. The absorbance was then measured at 460 microns in the 10 cm quartz cell of a Hitachi Perkin-Elmer spectrophotometer model 139. This absorbance was compared with that of a series of standards.

Dioxane and ethanol were purified by distillation. $\text{Hg}(\text{SCN})_2$ was freshly prepared from reagent grade KSCN and $\text{Hg}(\text{NO}_3)_2$. Reagent grade $\text{Fe}_2(\text{SO}_4)_3$ was used. The water used to prepare reagents and standards was obtained from melted ice frozen from our purest water. Glassware was soaked for several days in HNO_3 and then rinsed with distilled water. Workers used polyethylene gloves and hair coverings. The work was performed in a new laboratory free of acid fumes, but

the air supply was not especially filtered.

This method was sufficiently sensitive to detect equivalent chloride in 75% of the third brines. The concentration of equivalent chloride in the first brines was about 1000 γ Cl/kg, in the second brines the concentrations had dropped to about 200 γ Cl/kg, while in the third brines the concentrations remained at about 100 γ Cl/kg.

A regression of the chlorine concentrations in the polar snows determined by neutron activation and by colorimetric photometry had a slope which indicated that the colorimetric method gave results that were three times higher than results obtained by the other method. As has already been discussed, it is believed that the freeze-concentration method yields brines which are deficient in metals. We analyzed the 1st, 2nd, and 3rd brine concentrates and the final ice from one sample by neutron activation and found that, not only was there evidence of some contamination during the freeze-concentration process, but that the results would also have to be corrected by a factor of about 1.1 to account for chlorine loss in the last ice phase. The total overall difference between the methods on an absolute scale was therefore about 3.3

The colorimetric method is believed to be less absolute than the neutron activation method in this instance because the former method is susceptible to interference by unknown amounts of reducing agents and to contamination during analysis. We do not believe that the colorimetric method gives true chloride concentrations in polar snows, but gives, instead, the sum of sample and reducing agents plus some contamination chloride. Part of these reducing agents seem to originate in the sample because they are concentrated in the brines by partial freezing. We therefore discarded the chloride results obtained by colorimetric photometry.

We determined chloride colorimetrically first, and then resorted to the more costly and time-consuming neutron activation techniques after it was found that sodium and chlorine concentrations did not balance. These observations illustrate the danger of using a non-absolute method to determine the concentrations of an element when the range of concentrations is completely unknown. Colorimetric methods for chloride in polar snows can be made useful only after the true concentration range has been defined by more absolute methods. The same may be true for sulfate determinations. It should be noted that we did not attempt a conventional colorimetric method for silicon, because we considered that method unreliable at concentrations of γ per kg in the absence of any absolute information.

O¹⁸ Determination

Oxygen isotopic measurements were carried out in S. Epstein's laboratory at the California Institute of Technology, using techniques developed there (EPSTEIN and MAYEDA, 1953).

COMPILATION OF DATA

The data are summarized in Table 7. Snow density assignments have been read from smoothed curves drawn through observations taken at different depths. The older age assignments are calculated from accumulations, corrected for compaction. The error of these assignments increases with age, and amounts to several decades in the oldest samples.

(Please insert Table 7 here.)

Lead values are averages of three to five determinations, excluding some grossly high values. As mentioned earlier, moderately high values have been included in the averages. The accuracy of these reported lead concentrations is independent of mass spectrometric measurements. The Pb^{208}/Pb^{207} ratio in the

TABLE 7. Compiled Data for Polar Snow

Sample #	Location	Depth (meters) Greenland, Aug. 65 - 3 Antarctica, Jan. 66 - 0	Density	Character	Age	Water Concentration (g/g)										δD (‰)
						H	Na	Cl	Mg	Ca	K	Li	Si	Fe	Al	
65-11	Virgin Trench Site	0.32	Bottom of Layer	-	Summer '65	1965	15	4.9	2.3	3	2.9	1.2	0.4	-	-	-22.6
65-14	50 km ESE Camp Century	0.84	-	-	Spring '65	1965	19	8.5	3.7	5	9.7	3.2	0.6	-	-	-26.4
65-15	-	0.74	-	-	Jan./Winter '65	1965	42	28	3.7	6	1.1	2	0.3	-	-	-27.5
65-16	-	0.84	-	-	Dec./Winter '64	1964	37	19	3.9	5	4.6	2.1	0.4	-	-	-24.2
65-17	-	0.57	-	-	Fall '64	1964	10	3.7	0.7	2	2.6	1	0.1	-	-	-28.1
65-21	45 km ESE Camp Century	0.51	Bottom of Layer	-	Spring '65	1965	25	4.4	2.0	3	1.1	1.2	-	-	-	-
65-24	1 km ESE Camp Century	0.30	-	-	Spring '65	1965	27	2.1	4.7	2	2.2	2	-	-	-	-
65-18	Virgin Trench Site	3.0	Center Wholeness	-	Composite	1962	14	-	-	(11)	19.37	(44)	-	-	-	-
65-19	80 km ESE Camp Century	5.8	-	-	-	1950	04	-	-	6	6.0	(4.6)	-	-	-	-
65-20	-	7.6	-	-	-	1959	15	-	-	4	5.8	(4.1)	-	-	-	-
65-21	-	10.4	-	-	-	1975	12	-	-	4	3.0	(4.1)	-	-	-	-
65-22	-	12.8	-	-	-	1952	12	-	-	4	2.6	(3.2)	-	-	-	-
65-23	Inclined Shaft Camp Century	13.1	-	-	-	1964	16	2.6	4.9	1	5.3	2.2	-	-	-	-28.6
65-25	-	23.2	-	-	-	1973	04	-	-	2.1	4.5	2.7	0.0	-	-	-28.5
65-26	-	32.6	-	-	-	1992	06	3.4	2.1	2	2.1	2.2	1.1	5.2	-	-30.0
65-4	-	41.5	-	-	-	1982	07	2.8	5.1	5	5.5	2.8	-	-	-	-27.8
65-5	-	46.1	-	-	-	1981	03	2.0	3.1	5	5.5	2.8	-	-	-	-28.5
65-7	-	57	-	-	-	1959	04	1.0	3.7	5	2.4	2.9	0.0	-	-	-29.7
65-8	-	67	-	-	-	1952	05	2.0	2.0	7	6.0	3.1	2	2.9	-	-21.4
65-11	-	75	-	-	-	1955	03	2.1	3.1	8	9.4	2.1	-	-	-	-29.5
65-21	-	100	-	-	-	1952	01	2.0	1.0	5	6.0	2	0.6	-	-	-30.0
65-26	Ice Tunnel Camp Century	-	-	-	-	800 BC - 600	2.0	3.0	4.0	1.0	1.0	0.6	2.1	-	-	-
66-1	Virgin Trench Site	0.3	Bottom of Layer	-	Summer '65-66	1966	0.004	2.1	3.1	1	1.5	1.4	-	-	-	-
66-2	215 km NE Bird Station	1.0	-	-	Winter '65	1965	02	1.6	2.9	2	0.5	0	-	-	-	-
66-3	125 km NE Bird Station	0.5	Bottom of Layer	-	Winter '65	1965	9	-	-	2	1.2	1.2	-	-	-	-
66-7	35 km NE Bird Station	0.4	-	-	Winter '65	1965	2	-	-	2	0	2	-	-	-	-
66-9	Virgin Trench Site	4.4	Center Wholeness	-	Composite	1955	01	-	-	1	0	1.6	-	-	-	-
66-8	215 km NE Bird Station	5.4	-	-	-	1954	0.004	-	-	9	1.5	1.4	-	-	-	-
66-5	-	12.0	-	-	-	1964	0.004	-	-	9	1.5	1.4	-	-	-	-
66-A-1	Inclined Shaft Bird Station	5.7	-	-	-	1962	01	3.1	6.0	4	1.5	1.3	0.2	-	-	-
66-A-2	-	11.0	-	-	-	1974	0.005	-	-	1	1	1	-	-	-	-
66-A-3	-	15.6	-	-	-	1991	0.01	-	-	2	1.1	1	0.0	-	-	-
66-A-4	-	24.2	-	-	-	1951	0.01	2	1.6	2	0.0	1.3	-	-	-	-
66-A-5	-	28.5	-	-	-	1954	0.004	-	-	3	1.5	1.4	-	-	-	-
66-A-7	-	30.7	-	-	-	1951	0.009	-	-	3	1.1	1.3	-	-	-	-
66-A-8	-	31.6	-	-	-	1951	0.009	3.9	6.0	4	1.5	1.4	-	-	-	-
66-A-9	-	36.5	-	-	-	1951	0.01	-	-	2	1.1	1.0	0.1	0.4	-	-
66-A-10	-	43.4	-	-	-	1954	0.01	-	-	6	2	2.1	-	-	-	-
66-A-11	-	43.4	-	-	-	1954	0.01	-	-	6	2	2.1	-	-	-	-
66-1	Drum Glacier Tongue	-	-	-	-	-	-	-	-	5	1.1	1.1	0.4	-	-	-
66-M	Measure Glacier	-	-	-	-	-	-	-	-	14.2	14.2	1.1	1.4	-	-	-

Fig. 6 shows a number of values that are marked as "below detection limit".

All values are in grams per kilogram, not in percent, because analytical procedures were not well adapted to such high concentrations.

isotopic tracer was 500, and it changed to about 150 in snows containing smaller concentrations of lead. This change could be measured with an accuracy of about 2%. The first dithizone extraction yield could be measured with an accuracy of about 3%. Uncertainties in the known amounts of lead in the known blanks amounted to about 25% of the amounts present. Lead blanks from our containers could not be measured directly and were estimated on the basis of our experience with the procedures and knowledge of lead in salt and dusts and their concentrations in the snows. Lead concentrations in the 800 BC Greenland ice, and in most of the 17th, 18th, and 19th century Antarctic snows are reported as upper limits, using a variety of slightly different numbers, because the value of this container contamination is not well known. The uncertainty in positive results in the lower concentration ranges is about 30%, and this uncertainty drops to about 5% in the higher concentration ranges.

The atomic absorption sodium results were increased by the factor $[(\text{observed } \gamma/\text{kg}) \times 1.1 + 1]$ and then averaged with the neutron activation sodium results to give the final sodium concentrations listed in Table 7. The answer by each method was obtained by two or more determinations. The uncertainty in most of these concentrations is about 10%. Occasionally, as is clear from the sodium-chlorine imbalance for a few samples, the error may be larger. All of our reported sodium concentrations may be slightly low ($\sim 10\%$), but we are unable to determine the exact factor or the cause.

The origin of the largest error in the neutron activation chlorine data is the uncertainty in the polyethylene carboy contamination correction, which is an arbitrary minus 5 γ Cl/kg snow. This could have been underestimated by as much as 50%. Furthermore, it is likely that contamination from the carboys varied.

This uncertainty, plus counting errors, suggests that the error in the chlorine data is about 10%. The error in some instances may be larger. All values are the result of two or more determinations.

All atomic absorption magnesium results, which were obtained from duplicate runs, have been increased by the factor [1.6] obtained from isotope dilution checks on loss in the ice phase. The uncertainty in this large factor, which is probably different for different samples, places a large error on the magnesium results. It is about 20%.

Uncertainties in the isotope dilution calcium and potassium concentration results, all obtained from two or more determinations, are probably not caused by mass spectrometric errors. The $\text{Ca}^{44}/\text{Ca}^{40}$ ratio changed from 90 to 20, and this change could be measured with an accuracy of about 2%. The $\text{K}^{41}/\text{K}^{39}$ ratio changed from 80 to 2, and this change could be measured with an accuracy of about 2%. The greatest uncertainty lay in the extent to which these changes were affected by unknown contributions of calcium and potassium in the spectrometer source during an analysis. The effects of mass fractionation and discrimination were minimized by using a standardized analytical technique, and by partially canceling these effects out in concentration computations. The uncertainties in the calcium and potassium results are about 10%. There are special instances where the error is probably much greater. Sample 65-18 is almost certainly contaminated by frozen perspiration. Its handling suddenly proved awkward in the field, and it was severely handled and was difficult to trim clean. We believe that calcium is about 50% too high, and potassium is about 500% too high. Such a ratio is permissive in sweat. Samples 65-19, 20, 21 and 22 suffered excess handling also, but not to the severe degree as for 65-18, because they did not

tear loose from the tongs. Calcium in those samples is probably not more than 10% high because of handling, but potassium is still about 100% high because of perspiration contamination. The ratio of potassium to lead in perspiration is much greater than 20, which is the observed ratio in the samples, and the lead values are therefore unaffected by this amount of sweat contamination. This is proved by the lack of correlation between perspiration potassium contamination and lead concentrations. Lead is not unusually high in sample 65-18 compared to samples 65-19, 20, 21 and 22 nor in sample 66-A-9 compared to samples 66-A-8 and 66-A-10 (66-A-9 is probably contaminated by frozen perspiration or nasal mucus). All that is required to cause these effects is for a few drops of nasal mucus to fall on the ice or for small fragments of frozen perspiration to slip through a tear in a plastic glove and adhere to an ice block sample. Woolen gloves and shirts were worn for weeks, and the fibers became saturated with salt which contaminated the perspiration vapor freezing on the surfaces of plastic suits and gloves in contact with the fibers.

All of our observed titanium results, obtained from two or more runs, are probably low, because some titanium may have been firmly locked up in a silicon matrix and could not equilibrate with the tracer; some may have been scavenged by an oily film adhering to the walls of the melting drums, or some may have adsorbed onto the walls of the water bottles. We have no accurate correction factors to apply for these effects because of the cursory nature of the experiments, but judging from the results in Table 5 most errors could be approximately compensated for by increasing all titanium concentrations two-fold. This was done. These corrected data are listed in Table 7. The reported absolute concentrations have an uncertainty of about a factor of two. Errors in relative differences among

samples are probably smaller.

Silicon concentrations in Greenland ices are probably correct to within 30%. The silicon concentration reported for Antarctic ice is correct only to an order of magnitude. The main source of error in the Greenland ices is in the spectrographic technique, because contamination effects are small and amount to 10% at most. Uncertainty in contamination is the principal source of error in the Antarctic ices, but the reported value should be approximately correct because it checks with the titanium concentrations and the sea salt ratios of magnesium, calcium, and potassium.

There was concern whether appreciable amounts of metals were adsorbed on the polyethylene containers from the sample waters during aging, causing low results. The neutron activation results for sodium were obtained one year after the atomic absorption results, using the same solutions from identical bottles, and higher values were obtained at later times. Similar findings were obtained for calcium and potassium. We could find no evidence for this effect on lead. We found evidence for, and quantitatively measured a positive adsorption effect for silicon, although it was minor. We arbitrarily assumed a relatively large correction for a positive adsorption effect in the case of titanium. There is no reason to believe that we have failed to adequately consider and compensate when necessary for this effect, and that our results are in serious error because of it. There is every reason to believe that our remaining aged sample waters, which have been shipped to other laboratories for referee analyses, can be considered trustworthy from the standpoint of wall adsorption and contamination when provisions are made for the above factors.

INTERPRETATION OF THE DATA

The composition of sea salts and terrestrial dusts in polar snow

We use the term "sea salt" for the total mixture of soluble alkali and alkaline earth halides, carbonates, sulfates and nitrates existing in snow. This is a good approximation because only small amounts of soluble atmospheric salts found above the continents at temperate latitudes manage to work their way to polar regions. This latter type of salt contains very much more potassium, calcium, and sulfate than typical sea salt. Observed soluble salts in polar snows seem to be slightly enriched in potassium and calcium when compared to normal sea salt concentrations predicted from observed sodium chloride concentrations, but this effect may arise from our slight underestimation of sodium concentrations.

The evidence is as follows. In Table 8 are listed three successive sets of averaged, observed concentrations of Na, Cl, Mg, Ca, K, Ti and Si. The first set is an average of four different whole-year composites from New Byrd Station. The second set is from Camp Tuto ancient coastal glacier ice. The third set is an average of ten different whole-year composites from Camp Century. Sea salt contributions of normal composition calculated from the sodium present have been subtracted from all the totals. The remainders were ignored if they were within measurement error. Virtually all the alkalis and alkaline earths in the first set originate from sea salts. In the second set, the dusty remainder is large enough to provide a measurable calcium residue. In the last set, a major portion of all the metals analyzed, except sodium, originates from terrestrial silicate dusts. There are inconsistencies among the compositions of the dusty remainders obtained in this fashion which lie outside experimental error. The same dust in Camp Tuto and

Camp Century ices has a three-fold difference in the proportions of potassium and calcium. Antarctic dust is inexplicably high in potassium.

(Please insert Table 8 here.)

These problems disappear if the observed sodium concentrations are increased 10%, suggesting that this effect could be explained on the basis of experimental bias. Our neutron activation sodium concentrations appeared slightly low compared to spiked samples, but we were unable to evaluate a correction factor. An addition of potassium and calcium enriched salts from lower latitudes is an unlikely explanation because we observed the same enrichment effect in near-coastal regions where salt concentrations in snows are more than an order of magnitude greater than in the interior. Rather than believe that sea salts in snows are slightly fractionated compared to sea salts in oceans, we believe our reported sodium concentrations may be slightly low.

The chemical composition of the dusty remainder in snows from Camp Century is closely defined by the third set of data in Table 8. Although montmorillonite and illite clays could provide the observed magnesium, and illite and kaolinite clays could provide the observed potassium, few common clays could provide the large amount of calcium that is present. The observed chemical composition of the dusty remainder can be accounted for if it is assumed to consist of the mineral equivalents of soil derived from one part limestone and three parts shale, that is, considerable amounts of limestone dust have been mixed with regular clays. This is shown in Table 9. The high potassium content precludes any appreciable bulk contribution by meteoritic material to Greenland snows. The Tuto data eliminates the possibility of sea salt fractionation accounting for high potassium so as to permit

Table 8. Averaged Concentrations of Elements in Annual Composites (γ, kg)

		Na	Cl	Mg	Ca	K	Ti*	Si*
Average of 1942, 1857, 1775 and 1694 from Byrd Station.	Observed	32	59	4	1.3	1.6	0.01	0.4
	Calc. Sea Salts on Na basis	32	57	4	1.2	1.2	0.00	0.0
	Dusty Remainder	-	-	-	-	0.4	0.01	0.4
890 BC Coastal Glacier Fram Tuto.	Observed	350	570	45	17	16	0.06	2.1
	Calc. Sea Salts on Na basis	350	630	42	13	13	0.00	0
	Dusty Remainder	-	-	-	4	3	0.06	2.1
Average of ten composites: 1753, 1815, '35, '59, '81, '92, 1900, '33, '46, and '65 from Camp Century.	Observed**	20	39	5	6.4	2.7	0.1	6.8
	Calc. Sea Salts on Na basis	20	36	2	0.8	0.8	0.0	0
	Dusty Remainder	-	-	3	5.6	1.9	0.1	6.8

* Generalized from typical analyses.

** Excluding 1946 Mg value.

appreciable bulk contribution by meteoritic material. These arguments do not apply to Antarctic snows, where terrestrial silicate dust contributions are much smaller. It can be assumed that silicon is about 20% by weight in the terrestrial dust present in Camp Century ice. On this chemical basis, we observe the dust level to be about 35 γ /kg in Camp Century snows.

(Please insert Table 9 here.)

Variations of the amounts of salts and dusts in polar snows with season, locality and time

It seems likely that there may be repetitive, seasonal fluctuations by factors of two or three in the concentrations of dusts and salts in NW Greenland snows. For the single year whose separate snow layers were studied in Greenland, sea salt concentrations showed a marked decrease in the Spring and Summer, while terrestrial silicate dust concentrations, on the contrary, showed a distinct maximum in the Spring. This is illustrated in Figure 3. This same Spring snow layer was collected and analyzed 45 km away to the WNW, and at Camp Century, 80 km WNW. As shown in Table 10, characteristically high dust concentrations and low salt concentrations were also observed in this layer at these two locations.

(Please insert Figure 3 here.)

(Please insert Table 10 here.)

HAMILTON and LANGWAY (1967) observed cyclic variations in "Coulter" particle counts in Greenland snows, with particle maxima occurring near O^{18} minima in the stratigraphic section. We observe a salt maximum in the winter closely followed, but well separated, by a dust maximum in the spring. As can be seen from Figure 3, we observe a one-to-one correlation between salt content and O^{18}

Table 9. Relative Amounts of Elements in Snow Dusts and in Rocks

	<u>K</u>	<u>Ca</u>	<u>Mg</u>	<u>Ti</u>	<u>Si</u>
limestone (wt %)	0.3	30	4.8	0	2.4
shale (wt %)	2.7	2.2	1.5	0.4	27
1 (ls) + 3 (sh) (wt %)	2.1	9.2	2.3	0.3	21
observed (γ metal/2kg snow)	3.8	11	6	0.2	14

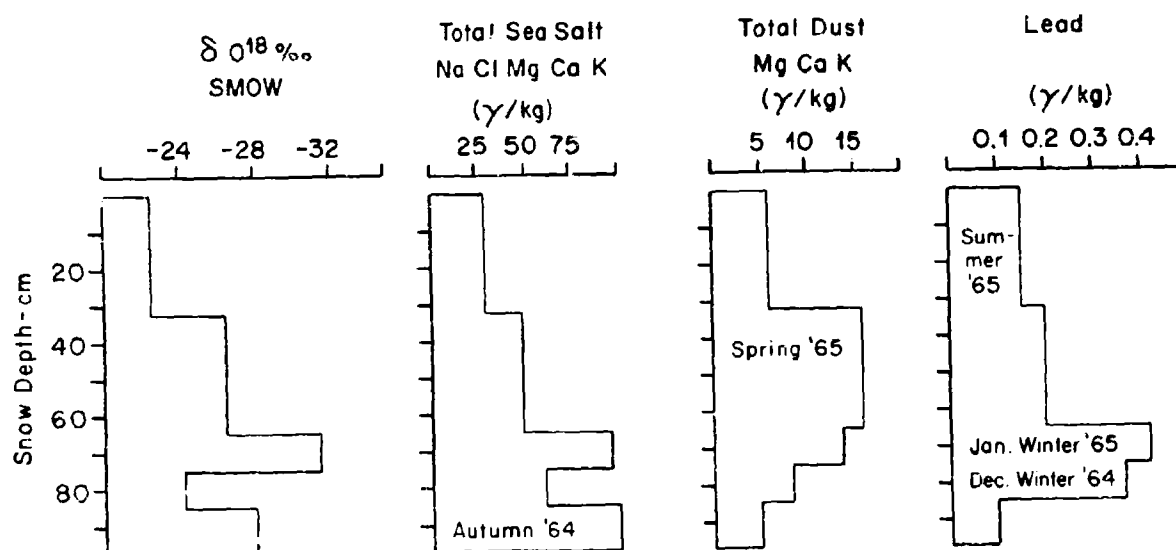


Figure 3: Seasonal variations in salt, dust and lead concentrations in snow during August 1964 to August 1965 at virgin site 80 km ESE of Camp Century. Silicate Mg, Ca, and K obtained from differences between observed total concentrations and sea salt portions. The latter were obtained by normalization from observed sodium and chlorine concentrations.

Table 10. Salt, Dust, and Lead in the Spring, 1965

Snow Layer at Three Different Locations				
Location	Position of layer from surface (cm)	Sum of Sea Salt Na, Cl, Mg, Ca, K (γ/kg)	Sum of Dusty Mg, Ca, K (γ/kg)	Lead (γ/kg)
Virgin Site (80 km ESE from Century)	32 to 64	48	16	0.19
Trail Site (45 km ESE from Century)	25 to 51	26	14	0.20
Camp Century	18 to 36	<u>67</u>	<u>27</u>	<u>0.27</u>
Average for '65 Spring Layer		47	19	0.22
Average of 10 whole year composites at Camp Century (1753 to 1965)		62	11	-

content (temperature), but do not observe any close relationship between temperature and dust content. Hamilton and Langway observed that particle maxima occurred after deepest winter, so perhaps qualitative agreement exists between our data and theirs.

Our observation that salt concentrations are higher in winter than in summer snows in NW Greenland agrees with observations by LANGWAY (1967), who found higher conductivity values in Fall than in Summer layers in Greenland ice cores, with observations of ZHAVORONKINA (1958), who found concentrations of sodium and chlorine in snow and rain to be higher in winter than in summer over central Russia, and with observations by DE BARY and JUNGE (1963), who found chlorine to be three times higher in winter than in summer precipitation at remote stations in northern Sweden. The latter region should be relatively free of industrial pollution effects. Our observations that salt concentrations in snow drop by more than a factor of ten in going from Camp Tuto, which is near the coast, to Camp Century, which is 120 km away from the coast, is in good agreement with the observed rate of decrease of salt content in precipitation at lower latitudes as a function of the distance from the coast (JUNGE, 1963). Salt concentrations in precipitation drop about a factor of ten within 100 km of the coast in temperate regions, CADLE'S (1966) statement to the contrary notwithstanding.

Our sample of Camp Tuto ice was 3000 years old. It came from the W edge of the Thule lobe, which is probably fairly stagnant, but even at a flow rate of 10 meters/yr, the accumulation zone would have been only 20 km E up to the spine of the Thule lobe, and then 10 km further NE up the flow path. From this point the unfrozen summer sea would have been about 20 km away to the SE. On the basis of our data, one would predict that salt concentrations should decrease

in the Tuto ice tunnel, in moving forward from our sampling location to the tunnel entrance, because such a direction is down section, and the age appears to increase greatly before the silt-contaminated shear zone is reached. Gow has already used conductivity measurements as a substitute for chemical determinations of chlorine and sodium in Ross Ice Shelf cores as a chronometric indicator (GOW, 1968).

Precise positioning in the stratigraphic column is required if a series of composite samples spanning less than 2 years' accumulation are to be collected and compared. Unfortunately, the importance of this effect was unknown when our samples were collected, and samples taken at Camp Century each covered a span of 1.2 to 2 years at unknown and consequently different times within those years. The scatter in salt concentrations observed in whole-year ice composites is ascribed largely to this artifice in collection. At New Byrd Station the annual layers were thinner, but the sample ice blocks were of the same size as in Greenland, so each sample covered a more favorable span of 2 to 4 years. The scatter of observed salt concentrations was therefore considerably greater in the Camp Century data than in the Byrd Station data, as shown in Table 11.

(Please insert Table 11 here.)

Just as there are seasonal fluctuations in dust and salt concentrations, there are probably somewhat milder fluctuations on a year to year basis. In view of this known and likely scatter, it is unlikely that increasing or decreasing trends in concentrations covering less than a factor of two could be observed. In Figure 4, no trends greater than 50% seem evident over a span of two centuries in the concentrations of salt and dust in polar snows.

Table 11. Comparison of Scatter of Sea Salt Concentration in Whole Year Composites

<u>Location</u>	<u>Mean Sea Salt Concentration</u> (Na, Cl, Mg, Ca, K)	<u>Limit of Scatter from</u> <u>Mean Regression</u>
Camp Century (10 composites)	62 γ /kg	+40% to -35%
New Byrd Station (4 composites)	98 γ /kg	+16% to -29%

(Please insert Figure 4 here.)

Our data show that the absolute amounts of sea salts and terrestrial silicate dusts are exceedingly small in polar snows; that snow from Byrd Station region is twice as salty as snow from the NW interior of Greenland; and that there is only one tenth as much dust in Byrd Station region snow as in NW Greenland snow. These observations accord with the overwhelmingly greater land area exposed at high latitudes in the north and the greater expanse of open ocean at high latitudes in the south. Although our Greenland data agree with well-known observations that coastal precipitation contains much larger amounts of sea salts than interior precipitation, we find less dust in coastal snows, even though the coast has a rocky, ice-free strip 20 km wide. The mantle of Arctic dust must have originated from distant sources in order to be so uniform. In coastal regions where salt concentrations are extremely high, salts might occasionally substitute for silicates as the massive center nuclei of snowflakes thus reducing the concentration of silicates in snow. All of these observations are summarized in Table 12.

(Please insert Table 12 here.)

Comparison with data obtained by other investigators

Polar snows are so pure they are difficult to properly collect and analyze. As shown by the examples in Table 13, which are not exhaustive, the disagreement among published data is extensive. Part of the data can be unified on the basis of a single interpretation, and it can be shown that the conflicting data which remains may be in error because of contamination.

(Please insert Table 13 here.)

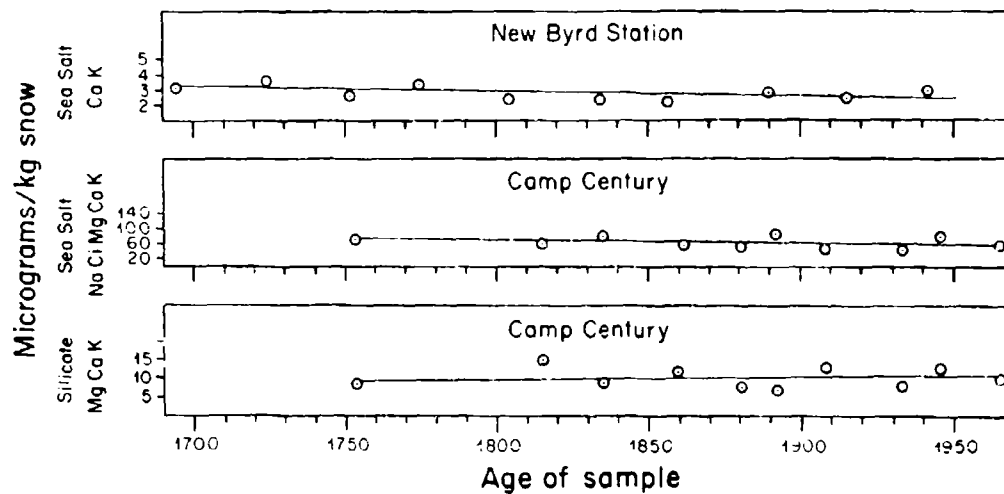


Figure 4: Variations of salt and dust in whole-year composites of firn with time at Camp Century. Scales are adjusted so that height of value at 1753 AD is same in all three graphs.

Table 12. Average Concentrations of Sea Salts and Silicate Dusts in Polar Snows

<u>Location</u>	<u>ppb Sea Salt*</u>	<u>ppb Dust**</u>
Antarctic Interior (Byrd Station)	110	2
Greenland Interior (Camp Century)	67	35
Coastal Greenland (Camp Tuto)	1100	10

* Calculated on the basis of normal $\text{SO}_4^{=}$ and $\text{CO}_3^{=}$ content.

** Silicon contents x 5.

Table 11
Comparison of Magnitude Differences, Log Scale Differences, and Agreement Among Geochronological Data for Polar Sites

Sample	Description	Test Concentration (ppm)							Reference
		Na	Cl	Ca	Sr	Th	U	Pb	
Greenland Region									
This work	For D-1 Core Average of 1930-1937	20	29	5	6.4	2.7	6.8	400000	35 ¹
Company 1961	Sealed Snow 1960-61	125	348	15	45	47	73	170	400 ²
July 1960	For D-1 Core Average of 1930-1937	29	27	-	35	11	-	250	-
For D-1 Core	Average of Several Years	20	40	-	100	30	-	100	-
For D-1 Core	Average of Several Years	25	-	8.4	9.0	8.2	-	-	130 ³
For D-1 Core	Average of Several Years	-	-	-	-	-	-	-	60 ⁴
For D-1 Core	Average of 1930-35	-	-	-	-	-	-	-	130
Antarctic Region									
This work	Antarctic Basin, Core 1000 m, 1960-1961	130	372	45	17	16	7.1	-	10 ⁵
Greenland Data 1960	For D-1 Core, 1000 m, 1960-1961	120	206	-	-	380	-	-	-
Greenland Data 1960	For D-1 Core, 1000 m, 1960-1961	250	-	25	17	29	-	-	-
Greenland Data 1960	For D-1 Core, 1000 m, 1960-1961	1300	6300	610	490	-	-	800	-
Greenland Data 1960	For D-1 Core, 1000 m, 1960-1961	170	310	45	170	-	-	180	-
Antarctic Region									
This work	Antarctic Basin, Core 1000 m, 1960-1961	12	59	4	1.3	1.8	0.4	160000	2 ⁶
Greenland Data 1960	For D-1 Core, 1000 m, 1960-1961	147	330	181	152	-	-	410	-
Greenland Data 1960	For D-1 Core, 1000 m, 1960-1961	8	-	-	-	-	-	-	-
Greenland Data 1960	For D-1 Core, 1000 m, 1960-1961	18	27	-	-	7	-	-	-
Greenland Data 1960	For D-1 Core, 1000 m, 1960-1961	30	-	4.9	8.0	3.1	-	-	140 ⁷

¹ Data from 1960-1961
² Data from 1960-1961
³ Data from 1960-1961
⁴ Data from 1960-1961
⁵ Data from 1960-1961
⁶ Data from 1960-1961
⁷ Data from 1960-1961

In agreement with our observations that more salt exists in New Byrd Station snow than in Camp Century snow, M. KUMAI (personal communication) also finds a greater number of entrapped giant salt particles in snowflakes at New Byrd Station than at Camp Century. Using sodium as the principal indicator of sea salt, our observations that salt concentrations are low in the interior of Greenland agree with those of Junge, Rodriguez, and McCorkell shown in Table 13. Our observations that salt concentrations are low in the interior of the Antarctic agree on this same basis with those of Hanappe et al., and Wilson and House. The evidence for the existence of this washout phenomenon at temperate latitudes is so strong that one would expect that similar washout mechanisms should also be operative in polar regions.

Our observations agree with those of Hanappe et al., and Sugawara that salt in polar coastal snow contains sodium, chlorine, magnesium, and calcium in nearly the same ratios as in sea salts. At present no investigator agrees with our observations that sea salts of normal composition occur in firn from the interiors of polar continents. These disagreements have been explained in the past as due to salt fractionation or to included terrestrial silicate dusts. Dusty and salty ices exist. We've studied two of them in the Antarctic. Such samples are of no general meteorological significance, however. Usually they are logistical artifacts, it being easier to set up and supply camps in dusty, atypical places. Catabatic winds keep coastal ices clean. We found that the clear, blue coastal ice at Tuto contained less dust than interior ice, and believe that this is generally significant. It is more likely that dust free ices should occur at Mirny and Roi Baudouin than at Tuto, for there is much less exposed land at the former sites. Hanappe et al. collected a snow sample at Roi Baudouin, using care to minimize contamination, and could not find the excessive

quantities of dust required by the data of Brocas and Delwiche. When we used care to minimize contamination at Tuto, we could find only 10 γ dust/kg ice instead of the 150 γ dust/kg ice found by LANGWAY (1967) ($\text{SiO}_2 \times 2.5$).

Wilson and Picciotto both pioneered experimental efforts to show that high salt concentrations do not exist within interior polar snows, and both exercised care to exclude contamination effects. In the first aim they succeeded, and our data verify their admirable efforts, but we do not agree with some of their interpretations. Hanappe et al., observed significantly higher concentrations of magnesium, calcium, and potassium over normal sea salt compositions on a sodium basis in snow from the Antarctic interior. Wilson and House found similarly high potassium concentrations. The former investigators explained the discrepancy as due to terrestrial silicate dusts, on the basis of their observed iron concentrations. The latter investigators explained the difference as caused by chemical fractionation of sea salts.

The explanation of Hanappe et al., disagrees with our dust data in the Rockefeller Plateau, for it requires an order of magnitude more titanium and silicon in the snow at Plateau Station than we observe at New Byrd Station. This seems highly unlikely. Concentrations of chemicals are observed to increase with decreasing rates of precipitation at temperate latitudes (JUNGE, 1963), but possible increases of dust concentrations at Plateau Station resulting from one-third smaller rates of precipitation should be compensated for by greater distances from dust sources. We believe that some of the alkalis and alkaline earths which Hanappe et al., observed in Plateau Station snows are probably derived from sea salts in normal proportions, while the rest originate from contamination. The fact that we observe these same elements to exist in significantly smaller concentrations but in sea salt proportions, and with dust contributions of these

same elements to be less than our detection limits in snows half-way between the sea and the center of the continent, suggests to us that the samples of Hanappe et al., which should be even less dusty, may be contaminated. PICCIOTTO and co-workers (private communication) maintain that we may be losing dust by adsorption on the walls of our melting drums, and getting only the soluble salt. HAMILTON (private communication) has analyzed drill core material from Byrd Station for particulate matter by counting and finds about three or four times as much dust as we do. We claim his material may be contaminated. He, like Picciotto, claims we may have lost some dust. Dust loss probabilities in our samples are discussed in the section describing the analysis for titanium. We do not deny that it is a factor that must be considered. We suggest that the iron value of Picciotto and co-workers may be too high because of contamination. Their latest (1968) observed nickel/iron ratios may still be excessive in relation to terrestrial values and may reflect meteoritic additions, contrary to their latest (1968) opinion, and in agreement with BROCAS' and PICCIOTTO'S (1967) earlier opinion, even though the (1967) opinion was based on erroneously high nickel values.

Contamination remains a problem, even when care is taken to exclude it. We are not aware of Wilson's collection procedure, but that of Picciotto's is known to us. Picciotto did not use polyethylene gloves or clothing while collecting, and his samples are susceptible to contamination from entrainment and creep from chemically impregnated gloves and clothing to the outside of the apparatus, and from there to the inside. We contaminated 5 samples in Greenland with alkalis, probably from frozen precipitation because an unexpected handling problem

developed in the field, and we also contaminated 1 sample in the Antarctic with alkalies, probably with nasal mucus or frozen perspiration by unknown accident.

Wilson and House do not show a chlorine-sodium balance, nor do they report the concentrations of a silicate dust index element. Their potassium values are higher than those of Hanappe et al., so that their dust requirements are less credible. We do not consider their sea salt fractionation explanation justified in view of our data.

We did not measure sulfate, but the fact that our data adhere closely to sea salt compositions, except where dust is known to interfere, suggests that published data for sulfate concentrations in continental polar snows may be grossly high. $\text{SO}_4^{=}/\text{Cl}^-$ ratios in rain approach 10 over the centers of continents at temperate latitudes, compared to the seawater ratio of 0.14 (JUNGE, 1963). This ratio remains higher than 0.14 in marine rain (DE BARY and JUNGE, 1963; JUNGE, 1963). In the mid-Pacific, SO_2 gas concentrations are equivalent to about $0.5 \gamma \text{ SO}_4^{=}/\text{m}^3$ (JUNGE, 1957). Particulate $\text{SO}_4^{=}$ concentrations are somewhat greater at low altitudes and lower at high altitudes (JUNGE, 1957). Chlorine gas concentrations are about $1 \gamma \text{ Cl}_2/\text{m}^3$ (DUCE et al., 1965). Particulate Cl^- concentrations are greater at low altitudes and lower at high altitudes (DUCE et al., 1965). The ratio of gaseous SO_2 to particulate $\text{SO}_4^{=}$ in the atmosphere increases sharply as continents and habitated areas are approached (GEORGI, 1960; LODGE, 1960).

The high ratio of gaseous chlorine and oxides of sulfur to particulate chloride and oxides of sulfur permits appreciable variations to occur in the composition of rain because the gases can react with water. Rain therefore can be expected to exhibit a wide range of $\text{SO}_4^{=}/\text{Cl}^-$ ratios, and it does. Snowflakes,

on the other hand, may be little affected by gases because the thin crystallizing film of water in them would either be unable to absorb much gas or would tend to exclude gases upon solidifying. They would be expected to exhibit mainly the chemical composition of the particulate matter which became entrapped in the snowflakes from the air as they grew and fell. The major fraction of salt in snowflakes occurs as sparsely distributed giant particles, several microns in diameter, occurring in non-center-nucleating, trapped positions (KUMAI and FRANCIS, 1962). Such particles have a rather uniform composition at temperate latitudes, the $\text{SO}_4^{=}/\text{Cl}^-$ ratios in them adhering closely to the sea salt value in marine environments (JUNGE, 1957; LODGE, 1960). It might be expected, therefore, that giant sea salt particles entrapped in snowflakes forming at high latitudes would have a normal sea salt $\text{SO}_4^{=}/\text{Cl}^-$ ratio.

Small amounts of gaseous chlorine and oxides of sulfur, trapped in the large amount of solid ice of snowflakes, may or may not be significant compared to the small amount of solid sea salt also trapped in the snowflakes. If they are not, then our salt data suggest that published sulfate concentrations in polar snows may be nearly one hundred times too high.

Measurements in the atmosphere near Camp Century Greenland and McMurdo, Antarctica suggest that particulate sulfate salts may predominate over silicate and sea salt particulates, however (FENN, 1960; FENN, et al., 1963; FISHER, et al., 1968). Atmospheric particle counting and chemical analysis suggest about $0.4 \gamma \text{SO}_4/\text{m}^3$ in northern Greenland on the ice cap and perhaps somewhat lower concentrations near the coastal regions of Antarctica. Less than half the particle mass seems to be sulfate over Greenland, but more than half appears to be sulfate in Antarctica. Assuming Fenn and co-worker's data suggests a concentration of about $0.6 \gamma \text{silicate}/\text{m}^3$ air and that Robinson's data suggests $< 0.0005 \gamma \text{Pb}/\text{m}^3$ for ambient air, an atmospheric

silicate/Pb ratio of > 1000 is estimated. We observe the ratio to be 35γ silicate to 0.2γ Pb per kg snow, or 170 in snow. The disagreement is in the direction of low dust values in our work, but this may be misleading, since we observe a clear negative correlation between seasonal depositions of silicates and lead in snow. Contamination from local traffic may have affected the sulfate particle data. Fenn and co-workers would have avoided it only with great difficulty during their 10 hour sampling periods at Camp Century in the summer and they did observe a one hundred fold reduction in particle concentrations during a winter sampling period at that same locality. Fenn ascribes the difference to meteorology. We suggest that a difference in traffic may be responsible. The Antarctic sulfate particle data is so erratic that it too suggests contamination (21 out of 36 samples showed no detectable SO_4), but this could be merely an artifact of sensitivity.

Junge claims the error in his SO_4 determinations was only 30%, and that since he did not observe a two-fold increase in SO_4 content in polar snows during the interval 1915 to 1957 which should have resulted from a two-fold increase in the burning of sulfur-containing fuels, SO_4 pollution did not reach Greenland in detectable amounts. We found that lead pollution did. Our evidence does not support a high natural sulfate background in polar snows. The sulfate pollution experiment should be repeated, using more absolute analytical methods such as isotope dilution, gas chromatography, or neutron activation, rather than the relative methods used earlier. This experiment will be very difficult to carry out, but until it is done,

geochemists, after considering our data, will find it hard to believe nephelometric or similar type sulfate data for polar snows, regardless of their accordance or discordance with normal sea salt compositions.

In agreement with our observations that silicate concentrations are much lower in Antarctic than in Greenland snows, M. KUMAI (personal communication), finds that giant silicate central nucleation particles in snowflakes at New Byrd Station possess much smaller diameters, on the average, than at Camp Century. KUMAI and FRANCIS (1962) found the giant central nucleating silicate particles in Greenland snowflakes to have an average diameter of about 1 micron, and the average mass of the snowflakes to be about 8×10^{-6} gm. These approximate figures suggest a concentration of about 100 γ dust/kg, which does not seriously conflict with our data. Langway and Windom both found excessively large amounts of silicates in Greenland firn and ice cores, and McCorkell found excessive amounts in Greenland ice well water. Although he did not report it in his thesis, WINDOM (1968) tried, but could recover no silicates from New Byrd Station melted firn block samples. He used the same analytical techniques for both his Greenland and Antarctic samples, the difference being that he used frozen CRREL drill core material from Greenland, while we collected and supplied the melted Antarctic samples that he analyzed for both silicates and Pb^{210} . Windom's Antarctic samples had been melted for nearly one year before he analyzed them. The Antarctic samples may have been cleaner than the Greenland samples, and the silicates may have dissolved in the Antarctic samples. Both of these statements are probably correct.

Our silicate concentration data are in accord with HAMILTON'S and LANGWAY'S (1967) particle concentration observations in Greenland ices.

The latter investigators analyzed small, well-cleaned core fragments in a super-clean room. Their Coulter counter method would ignore soluble chemical contamination, which is probably an important source of excess chloride, alkalies, and alkaline earths. Their results would tend to be low because of silicate dissolution. The fact that both Hamilton and Langway and we observed seasonal variations in dust concentrations suggests that the data refer to natural, not artifact, dusts.

It is easy to contaminate drill cores with excessive amounts of dusts and chemicals. In some shallow drilling; ice tailings from mechanical drills are blown out of the holes with compressed air that is highly contaminated by oils, metals, and dusts from the machinery. When a thermal drill is used the highly contaminated melt-water which is hoisted out contaminates the cores. In deep drilling with mechanical drills, the ice tailings are melted and hoisted out. Generally, in deep drilling the upper permeable zone is cased off and the holes are kept filled with mixtures of technical grades of kerosene or glycol and ethylene dichloride, which may negate all chloride determinations. Melted tailings become highly contaminated after contacting the alloys and plastics in the drill assembly, and then contaminate the core. Cores become minutely cracked through pressure release and thermal and mechanical shocks, and impurities are forced into minute cracks which later anneal during storage. Such impurities are impossible to remove. Hand-augered cores are usually taken within permeable firm, which is easily contaminated to depths of a number of centimeters within a core because of its permeability and the gross uncleanness of the auger, extension rods, gloves, and clothing of the workers. It is therefore extremely difficult, if not impossible, to clean contaminated impermeable ice cores because

of entrainment creep by impurities and because of contaminated microfractures.

The cleaning of contaminated permeable firn cores is hopeless. E. PICCIOTTO (personal communication), observed about twenty times higher concentrations of sodium, magnesium, calcium, and potassium in the periphery than in the center of a cleaned ice core from New Byrd Station, and the center values were still excessively high. It is noteworthy that well water analyses show smaller degrees of sodium chloride contamination than cores do, apparently because of the huge volume of well water involved relative to the degree of contamination.

It may be difficult now for investigators to assign a general significance to our observations that sea salts are not fractionated in polar snows because of the influence of literature reporting analyses of contaminated drill core material using analytical methods more suited to river waters and temperate latitude rains.

To help eliminate some of these difficulties in the future, we agree that silicate dust concentrations should be checked by melting at least one sample only in the container in which it is finally analyzed. On the other hand, salt fractionationists should agree that two additional experiments should be carried out in future work: seawater should be diluted in such proportions as to give the predicted sodium concentrations the investigator claims to observe, and then that liquid should be analyzed for sodium, chlorine, potassium, calcium, magnesium, sulfate, and silicon to show that the investigator can observe correct sea salt proportions when they actually exist; and the investigator should analyze at least one shallow firn sample collected by hand with extreme precautions against

contamination from a virgin site in the region from which the bulk of the drill core samples originated.

Amounts of lead in polar snows

As shown in Figure 3, lead concentrations in Greenland snows are about twice as high in winter as in summer. This does not mean that seasonal variations in the concentrations of lead aerosols and sea salts coincide, because they do not. Out of three Winter and Autumn samples, the correlations between lead and sea salts were negative in two. There is a greater discordance between lead and silicate dusts, however, with the seasonal maxima and minima of each being clearly out of phase. Such fluctuations are probably not locally capricious, and may be annually repetitive. The uniformity of lead concentrations in the Spring, 1965, snow layer over a distance of 80 km, as shown in Table 12, conforms with this view.

Since each of the whole-year composites collected in Greenland covered one year plus a fraction, the observed lead concentrations in the different composites should vary according to the chance location of the sample in the stratigraphic column. Evidence that this factor has introduced scatter in the time trends of the observed lead concentrations is shown in Figure 5, where trends for salt, dust, and lead during the period 1815 to 1933 are given. This is the best century out of those studied to compare trends in concentrations because world industrial production of lead aerosols increased only by a factor of about three during it. If irregular locations of the 1.5 year samples in the stratigraphic column produced fluctuations in observed chemical concentrations, then lead concentrations could be expected to vary directly with salt and inversely with dust concentrations. This is observed to happen, as shown in Figure 5. The 1933

sample provides the only conflict with this view.

(Please insert Figure 5 here.)

O^{18} - Si relationships from Table 7 and Figure 5 neither refute nor verify this view, because out of two critical samples, 65-4 and 65-8, the first disagrees while the second agrees. The composite character of the whole-year samples renders them unsuitable for such a comparison in the face of such small isotopic variations of oxygen.

As shown in Figure 6, lead concentrations have increased twenty-fold in NW Greenland snows during the last two centuries and they had increased ten-fold during the eight centuries before, so that a general time trend is evident despite the artificial fluctuations introduced by the sample collection procedure.

(Please insert Figure 6 here.)

The observed upper limit of lead in 800 BC Tuto ice is above the 0.0001 γ Pb/kg level expected from natural terrestrial dusts present in the ice, on the basis of 12 γ Pb/gm dust (CHOW and PATTERSON, 1962), the dust being 10 γ /kg ice. At least half of the lead in NW Greenland snows originated from natural silicate dusts, and probably less than an equal amount originated from natural volcanic emanations or other natural exotic sources (CHOW and PATTERSON, 1962). The silicate dust concentrations in snows from Camp Century can be used to estimate the natural background of lead in those snows. At a dust level of 35 γ dust/kg snow, the natural lead level should be about 0.0004 γ Pb/kg snow.

Our measurement of lead in the oldest ice layer at Camp Century at 1753 AD corresponds to the beginning of the European Industrial Revolution (in production terms), and it can be seen that lead concentrations there at this date are already more than twenty-five times higher than natural levels. This addition

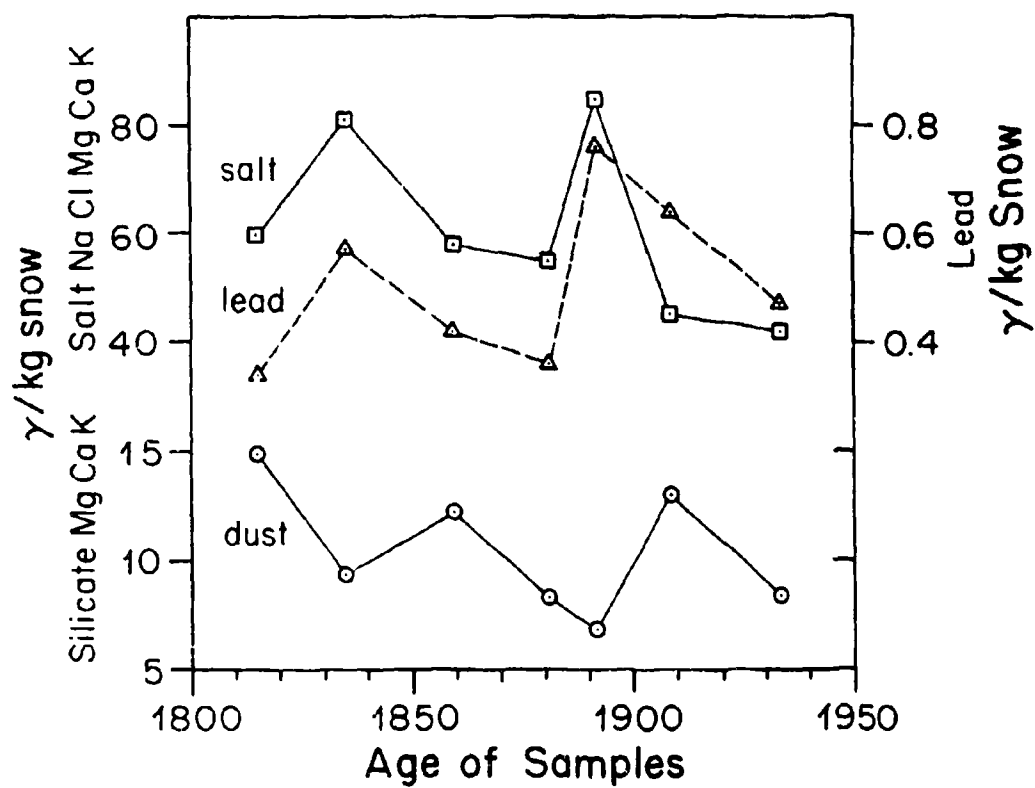


Figure 5: Positive correlation of salt-lead variations and negative correlation of dust-lead variations in whole-year composites of snow at Camp Century.

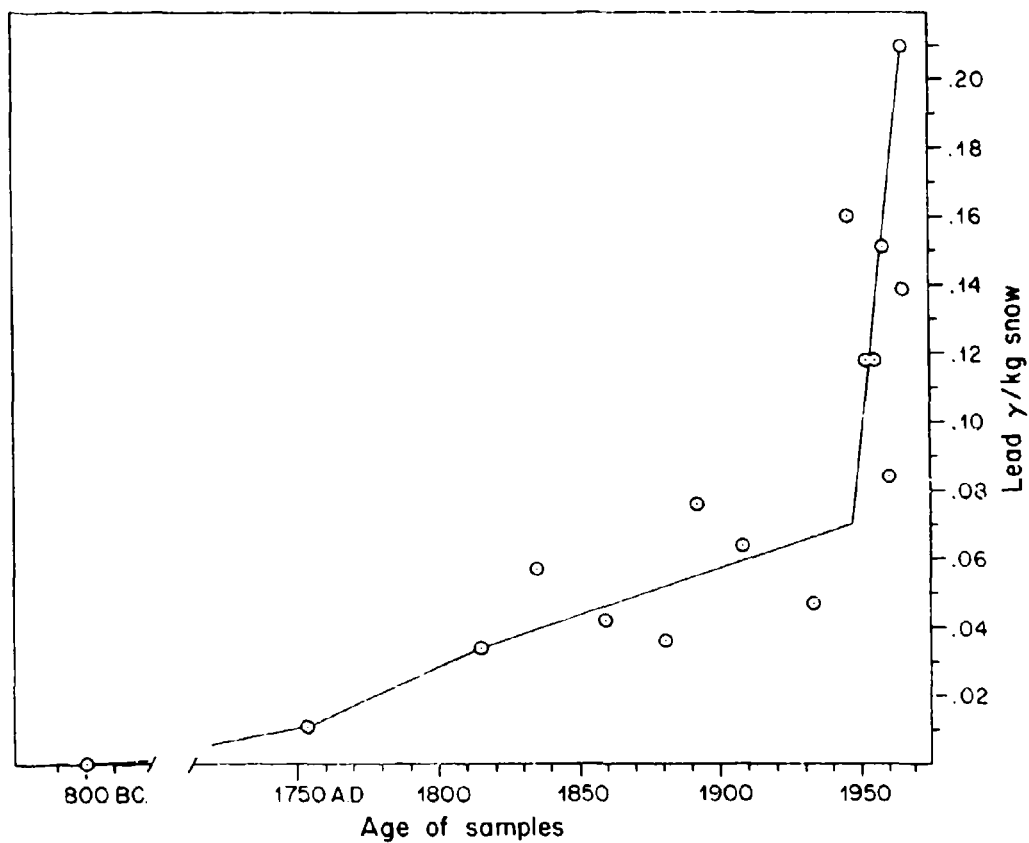


Figure 6: Increase of industrial lead pollution in Camp Century snow with time since 800 BC. Scale adjusted so that height of lead value at 1753 AD is same as height of salt and dust values at 1753 AD in figure 4.

of industrial lead probably took place following a minimum in European lead production at about 900 AD (PATTERSON, 1968). Lead concentrations apparently, tripled in Camp Century snows during the half-century, 1753 - 1815. They seem to double again during the following century, 1815 - 1933, although trends are difficult to discern among fluctuations caused by seasonal variations and collection of the samples from inconsistent locations in the stratigraphic column. During the next three decades, 1933 - 1965, lead concentrations arose abruptly by a factor of about three. Today, lead concentrations in Camp Century snows are well over five hundred times above natural levels.

The contrast between high levels of lead in Greenland snows and low levels in Antarctic snows is a prominent feature of the data. As can be seen in Table 7, the difference is greater than a factor of ten. We do not observe exactly the same trends on the Rockefeller Plateau as in Greenland because lead concentrations in Antarctic snows are near or below our ability to measure them. At a dust level of 2 γ dust/kg snow, the natural lead level should be about 0.00003 γ Pb/kg snow. Two samples from the early 19th century definitely contain at least 0.002 γ Pb/kg snow. Four samples later than 1916 definitely contain lead, three of them at least 0.01 γ Pb/kg snow. These observations suggest that increases in lead concentrations by more than a factor of three hundred have occurred in Antarctic snows during recent decades, but such changes are difficult to perceive because of measurement insensitivity and error.

No significance can be attached to the difference observed between lead concentrations in the upper and lower halves of the 1965 - 1966 snow layer, because correlation with stratigraphy is too crude. The enormously high concentrations of lead observed along the trail between Antarctic virgin site and New Byrd Station originate from local vehicular exhausts deposited when a network of posts

were installed at one mile intervals along a portion of the trail, to be used in future measurement of ice movement. They had been installed by investigators using leaded fueled vehicles during two previous years. We were forced to use this trail as a means of navigating quickly into the virgin upwind quadrant from New Byrd Station because back-sighting trail flags accurately is subject to time-risk from storms, and delayed supply transport from McMurdo to Byrd had seriously compromised our field program. Our virgin site was 45 km upwind and beyond the contaminated end of the strain-net trail (the trail to the virgin site in NW Greenland was entirely in virgin territory).

Sources of industrial lead in polar snow

Today the overwhelming source of atmospheric lead aerosols is automotive fuel (PATTERSON, 1965), but significant amounts of industrial lead aerosols apparently were introduced into the earth's atmosphere in the past by smelting lead ores. It has been suggested that contributions from other sources are relatively minor on a hemispheric basis today. These include the refining of lead scrap, the burning of buildings containing leaded ~~paints~~ and putty, the re-circulation by winds of soil contaminated by industrial lead, the burning of coal, the burning of trash containing industrially leaded materials, and the burning of foliage coated with fallout of burned lead alkyls (PATTERSON, 1965).

Lead has a low melting point, but the liquid metal also has a low vapor pressure, so that the smeltery injects lead aerosols into the atmosphere mainly because gases act upon finely divided materials at high velocity, not because lead is boiled away. At the beginning of the Industrial Revolution in 1750, large amounts of relatively coarse lead ore dusts were lost from the smelteries in addition to lead fume because of poor furnace designs and smelting procedures.

Such conditions were tolerated because ores were not scarce, and a primary aim was silver recovery. In the 19th century, furnace designs and smelting procedures had improved so as to eliminate the greater part of lead ore dust losses from smelteries. Worldwide losses of lead fume, or lead oxide-rich aerosols, were probably still severe at this time, however, because it was not until the late 19th and early 20th centuries that, in the face of a growing scarcity of ore and an increasing demand for lead, worldwide attention was paid to the recovery of economically valuable lead smelter fume. During that time worldwide lead fume losses from smelteries were reduced about a factor of 4. During the last four decades lead fume losses have been reduced by about a factor of 8. Much of this recovery involved coarser sized particles, however, so that the reduction in loss of sub-micron sized aerosols which migrated to polar regions was less. To summarize: from 1750 to 1880 the fraction of lead in ores lost on a worldwide scale as aerosol fume may have been about 2%; between 1880 and 1920 that loss may have been reduced to about 0.5%; today, such losses probably have been reduced to about 0.06%.

These figures are estimates. No published data exists. A private communication from the Lead Industries Association, Inc., suggests that today primary smeltery stack losses of lead may amount to 0.02% of the amount smelted, and that secondary smeltery stack losses of lead may amount to 0.15% of the amount smelted. Such figures are based on operations in the United States and Canada. According to a German source, flue purification efficiencies of solids from gas emissions from sinter, blast, and reverberatory furnaces vary from 96% to 99.5% (ANONYMOUS, 1961). We would have estimated primary smeltery losses to be higher than 0.02% and secondary scrap recovery smeltery losses to be

lower than 0.15% in the United States and Canada today. On a worldwide basis, it would not be far wrong to estimate total smeltery stack losses of lead today at 0.06%. These materials have passed through recovery apparatus, and consist of very fine aerosols.

About half to a third of the lead burned in automotive fuels is introduced into the atmosphere as long-lived finely divided aerosols (HIRSCHLER et al., 1957; MUELLER et al., 1964). Changes in such factors as the proportions of leaded fuels consumed in airplanes and in low and high compression engines, which determine the proportions of lead in fuel converted to atmospheric aerosols, are unimportant compared to the enormous increase in the total rate of burning of leaded fuels during the last four decades.

Listed in Table 14 are the amounts of lead smelted in the northern and southern hemispheres since 1750 AD and the amounts of lead burned as alkyls in the northern hemisphere during that same period. Lead smelter production data for 1890 - 1966 was obtained from the U. S. Bureau of Mines Mineral Yearbooks and earlier generic volumes. Except for 1966, figures are ten-year averages. The 1880 and 1860 data are obtained from lead metal production figures of SMITH (1929). The 1800 and 1750 data are based on silver production data of PATTERSON (1968). At those early times published lead metal production figures underestimate total lead smelting rates by an order of magnitude. Peruvian production has been assigned to the southern hemisphere. It was significant in early times and was so close to the equator it probably introduced lead aerosols into different hemispheres in different years. Lead alkyl production data for 1924 - 1958 are from "Public Health Aspects of Increasing Tetraethyl Lead Content in Motor Fuel", U. S. Public Health Service Publication No. 712 (1959). Figures are for single years. The 1966 figure is from the Minerals Yearbook. The lead alkyl production data listed in Table 14

represent world production. They were obtained by adding 5% to 1940, 10% to 1950, 20% to 1958, and 40% to 1966 domestic United States lead alkyl production.

(Please insert Table 14 here.)

The trends in lead production are shown in Figure 7, but they cannot be directly compared with the trends of lead concentrations in snow at Camp Century shown in Figure 6, because of changing fractions of lead aerosol production in smelteries and because of the large fraction of lead aerosols produced by burning lead as alkyls. These factors are accounted for in Table 15, where the total amounts of lead aerosols produced/yr at different times in the next to last column are compared with observed lead concentrations in snow at Camp Century given in the last column.

(Please insert Figure 7 here.)

(Please insert Table 15 here.)

In order to compare the figures listed in the last two columns of Table 15, it must be assumed that lead aerosols annually deposited in snow at Camp Century represent a constant fraction of the amount of lead aerosols annually emitted into the atmosphere of the northern hemisphere. This is a poor approximation because of changing meteorological conditions and because the locations of principal lead smelteries have changed significantly with time, which has altered mean travel times and therefore washout fractions of lead aerosols migrating to the NW Greenland deposition site. The trend since 1750 has been for a substantial shift of lead smelteries to more northerly latitudes. This decreasing involvement in the north tropical meridional tropospheric circulation cell and an increasing

Table 14. 10^3 Metric Tons of Lead Smelted or Burned as Alkyls Per Year Since 1750 A.D.

<u>Date</u>	<u>Northern Hemisphere</u>		<u>Southern Hemisphere</u>	<u>Northern Hemisphere</u>
	<u>Primary Smelting</u>	<u>Secondary Smelting</u>	<u>Primary Smelting</u>	<u>Burned Alkyls</u>
1966	2400	700	350	310
1960	1900	600	360	180 (1958 data)
1950	1300	550	240	110
1940	1300	400	230	36
1930	1200	400	170	4
1920	880	200	110	0
1910	940	60	100	
1900	750	0	80	
1890	520		40	
1880	400		2 +	
1860	220		+	
1800	90		50	
1750	60		40	

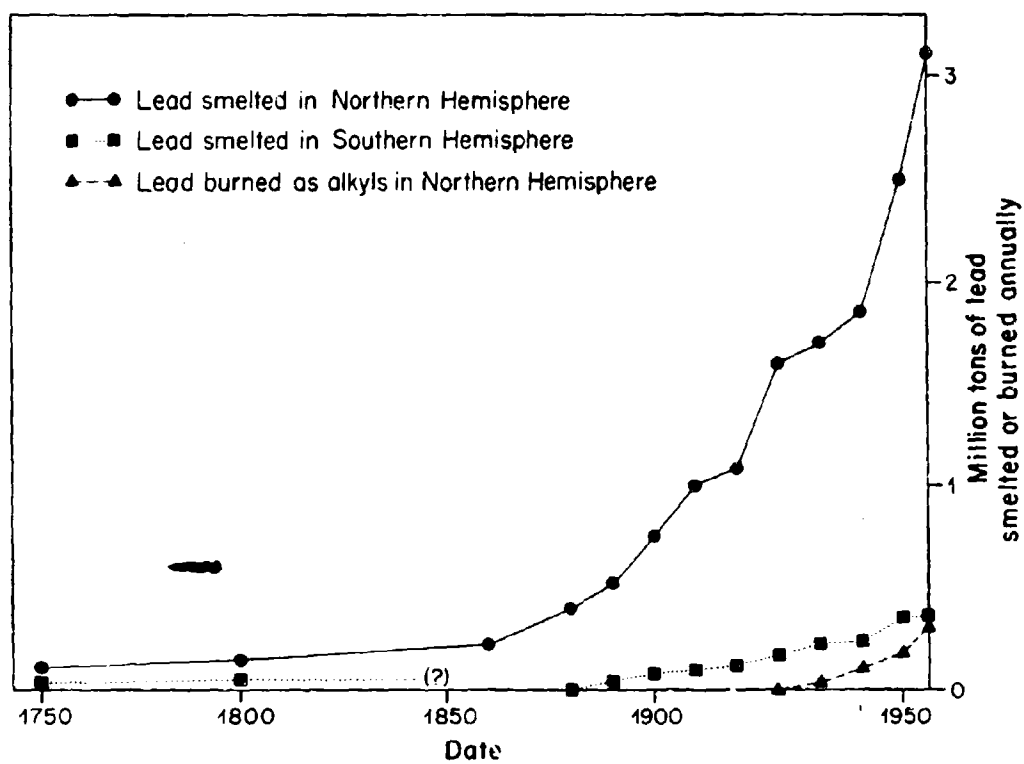


Figure 7: World lead smelter production and lead alkyl production since 1750 AD.

Table 15. Lead Aerosol Production in the Northern Hemisphere Compared with Lead

Concentrations in Camp Century Snow at Different Times

Date	10^5 tons of lead smelted/yr	fraction converted to aerosols	tons of lead aerosols produced/yr from smelteries	10^5 tons of lead burned as alkyls/yr	fraction converted to aerosols	tons of lead aerosols produced/yr from alkyls	total tons of lead aerosols produced/yr	γ lead per kg snow at Camp Century
1753	1	2%	2×10^3	-	-	-	2×10^3	0.01
1815	2	2%	4×10^3	-	-	-	4×10^3	0.03
1933	16	0.5%	8×10^3	0.1	40%	4×10^3	10×10^3	0.07
1966	31	0.06%	2×10^3	3	40%	100×10^3	100×10^3	0.2

involvement in the rising convergences of the middle latitude and polar meridional tropospheric circulation cells would tend to carry a larger fraction of lead aerosols more directly to polar locations. It is possible that this factor has significantly nullified the large decrease with time of the fraction of lead emitted as aerosols by smelteries. Upon comparing figures in the last two columns of Table 15, a surprisingly good correlation can be seen, considering the magnitudes of the various approximations involved.

The amount of lead deposited at Camp Century is reasonable compared to that expected from lead alkyls burned in the northern hemisphere. At an average concentration of $0.2 \text{ } \gamma \text{ Pb/kg}$ snow north of latitude 65° N and a mean accumulation of $20 \text{ gms of H}_2\text{O/cm}^2 \text{ yr}$ (BLAIR and FITE, 1957), the total amount of industrial lead aerosols deposited annually there should be about 1×10^3 tons, which is about 1% of the total annual lead aerosol production in the northern hemisphere listed in Table 15. 99% of the lead aerosols produced at temperate latitudes in the northern hemisphere should be washed out before they migrate to polar regions according to the following measurements: (1) the concentration of industrial lead in rain near urban areas in North America, ~~which characterizes~~ the atmospheric concentrations of lead aerosols in source regions, is about $40 \text{ } \gamma \text{ Pb/kg}$ (CHOW and EARL, 1968a; LAZRUS et al., 1969), and the concentrations of industrial lead in rural snow at temperate latitudes is about $2 \text{ } \gamma \text{ Pb/kg}$ (TATSUMOTO and PATTERSON, 1963b), while the concentration of industrial lead in precipitation in polar regions is about 1% of that in source regions, or $0.2 \text{ } \gamma \text{ Pb/kg}$; and (2) the standing crop of lead aerosols in the Arctic atmosphere at ground level is less than $0.0005 \text{ } \gamma \text{ Pb/m}^3$, while the standing crop of lead aerosols in the north temperate and north tropic atmospheres at ground level is

about $0.0015 \text{ } \gamma \text{ Pb/m}^3$ (CHOW, EARL, and BENNETT, 1969), and the volume ratio is ten, so the factor of > 30 obtained from these data agrees with a washout factor of 100 (Robinson's lead in Arctic atmosphere figure, as well as our lead in Antarctic atmosphere figure, is slightly high because unavoided traces of lead coming from the exhausts of planes or vehicles operating in the local vicinity have been included in them. In the Antarctic we could readily perceive the lead effects of a diesel-fueled C-130 landing or taking off when the air sampler was not turned off).

The ratio of lead to silicate dust is not greatly different in the Arctic and in temperate latitude precipitation. In the former case there are about $0.2 \text{ } \gamma$ of lead and $35 \text{ } \gamma$ of silicates in a kilogram of Arctic snow. In the latter case there are about $40 \text{ } \gamma$ of lead and 10 milligrams of silicates in a kilogram of temperate latitude urban rain. Silicates in rain were calculated on the basis of "excess" potassium over sea salt compositions in North American rain (JUNGE, 1958), assuming K_2O to be about 3% in silicates. In both instances the ratios are about 500 times greater than natural values.

The burning of coal has never been a significant contributor of lead aerosols in the atmosphere, even compared to the output from lead smelteries in the early Thirties. At that time about 1.3×10^9 tons of coal, which contained 10% to 20% ash and about 5 ppm of lead (CHOW and EARL, 1968b), were burned annually in the northern hemisphere (REVELLE and SUESS, 1957). About 1/5th of the leaded silicate ash from the coal was introduced into the atmosphere, but only about 5% of that ash consisted of long-lived finely divided aerosols. Although in modern pulverized coal burning furnaces, 80% of the ash finds its way into the flue gas, more than 99% of this is now removed by electrostatic precipitators

(FIRST, 1968). Because of volatility and melting point differences, lead probably was more readily introduced into the atmosphere than silicate ash by a factor of about two. In the early Thirties, therefore, about 100 tons of lead were introduced as traces in silicate ash aerosols into the atmosphere of the northern hemisphere from burning coal each year compared to the 8000 tons of lead oxide-rich aerosols originating from smelter fume and the 4000 tons coming from automobile exhausts. Coal contributions of lead aerosols could have been greater by an order of magnitude, and they would still have been minor. In later years, the increased emission of ash from growing public utility plants was cancelled by an increased use of ash-collecting devices plus an enormous increase in the rate of burning lead alkyls.

JAWOROWSKI (1967), suggests that lead contributions to the atmosphere from coal ash and burning lead alkyls are about the same. We observed that the concentrations of lead pollutant aerosols in Greenland snows rose 300% after 1940, when lead alkyls were burned in large amounts. This abrupt increase over-rides a 40% concurrent increase in the burning of coal, and clearly demonstrates that Jaworowski's view, which is also advocated by leaded fuel industries, is incorrect. Jaworowski was seeking an explanation for his failure to observe a sudden increase in lead concentrations in Polish glaciers after 1940. It has already been pointed out that his excessively high lead data may be of only local significance. His views on lead contribution from coal are based on unrealistically high estimates of lead concentrations in coal (200 ppm), and the fraction of coal converted to fine silicate aerosols (2%).

The low concentrations of lead aerosols observed in Antarctic snow agree with expectations, if they were produced mainly in the northern hemisphere, and

had difficulty migrating past the upward convergence of the northern and southern tropospheric meridional circulating cells. Some of the lead observed in the early 19th century snow at New Byrd Station could have originated from Spanish silver production centers in Peru.

These lead studies suggest that Greenland snows may be archaeologically important concerning the intensity of man's industrial activities, especially during Roman times and the Medieval Period. We urge that consideration be given to this point, and that a considerable fraction of the enormous effort now devoted to the Antarctic be diverted to Greenland, which is not only of greater archaeological interest, but is scientifically simpler and logistically cheaper to study.

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